Analysis of Suspended Solids in River Water to Assess Their Role in Metal Transport

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بسم الله الرحمن الرحيم

In the Name of Allah, the Most Compassionate, the Most Merciful

محمد صلى الله عليه وسلم

إلى منارة **العلم** والإمام المصطفي إلى **الأمي الذي علم المتعلمين** إلى سيد الخلق إلى رسولنا الكريم سيدنا

My Mother and father

Love & Inspiration

الى امي وابي

شكر وحب وعرفان

Abstract

The contamination by metals present in surface water causes problems to human health. The ultimate aim of this work is to determine the role of fine suspended sediment to the transport of metals in rivers. During the work, the ability of fine suspended sediment to carry a range of metals in the river water in different seasons was measured in different samples.

Suspended sediment carries a substantial proportion of the metals in river water. The distribution of suspended particles is an important factor in controlling the availability of metals in the river water. Dissolved form, and adsorbed to the surface coating of suspended particulate matter are two ways to transport metals in rivers. Firstly, the work was carried out in the laboratory, using suspended sediment components, to assess metal uptake by different components, while later studies utilized natural suspended sediment to study metal transport in real situations. The water samples were taken for this research from tributaries of the River Kelvin; Craigton Burn, Allander Water, Craigmaddie, Glazert Water, Bothlin Burn, Luggie Burn, and Cameron Burn. The research tries to evaluate the concentrations of Ca, Fe, K, Mg, Mn, and Zn in suspended particles in these tributaries. The technique used two filters 1.2 µm and 0.2 µm to collect the suspended sediment from water samples. Some representative samples of kaolinite, bentonite, humic acid and iron oxides were used in the laboratory based studies to improve understanding the distribution of the heavy metals Cu, Pb and Zn between metals sorbed on the solid phase and metal `in the solution phase. The adsorption of the heavy metals Cu, Pb and Zn shows different response between these materials. In addition, the experiments were carried out to measure the distribution of copper, lead, and zinc between an aqueous phase and solid phase of mixed materials (composite) sediment.

The results demonstrate that the fluvial system is one of the major modes of dispersing and transporting metals from soil and parent rocks. The overall results indicated that the large and fine particle sizes carry significant metals concentrations in the river system. The investigation of the suspended sediment phases offers additional information and understanding of the movement and behavior of metals within river water. The concentration of the particles > 1.2 µm is higher than that in the fine particles 1.2 and 0.2 µm diameter.

The format of this thesis;-

Chapter (1) Introduction. This chapter introduces background information that is important to the research, such as the choice of metals, the suspended particulates, and the relationship between them. Chapter (2). This chapter describes the method used to prepare suspended sediment of the components; the sampling sites and the sampling techniques, and the sample

preparation and analysis process. Chapter (3). This chapter describes the different filter paper materials used in this study, and describes the analytical methods that were common with the different filter papers in the experiment. Chapter (4). This chapter describes the distribution of the heavy metals Cu, Pb and Zn between sorption in the solid phase and in the solution phase for single adsorbent system material and for a mixed adsorbent system. Chapter (5) This chapter explores the role of suspended sediment in the transport of metals in tributaries of the River Kelvin. Chapter (6) contains the Conclusion and suggestion for future work.

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Declaration

This thesis and research described here are performed entirely by the author except where expressly stated

Ibrahim .O. M. Matoug

ABBREVIATIONS

B	**Bentonite**
ETAAS	**Electrothermal atomic absorption spectrometry**
FAAS	**Flame atomic absorption spectrometry**
FDC	**Fast distribution coefficient**
GFAAS	**Graphite furnace atomic absorption spectrometry**
H	**Humic acid**
ICP-AES	**Inductively coupled plasma atomic emission spectrometry**
ICP-MS	**Inductively coupled plasma mass spectrometry**
IO	**Iron oxide**
K	**Kaolinite**
PZC	**Point of zero charge**
SdFFF	**Sedimentation Field Flow Fractionation**
SPLITT	**Split flow lateral transport thin fractionation**

Chapter 1
Introduction

1.1 Metals in the Environment

Metallic elements are part of our natural environment. Some are essential for living organisms in trace amounts such as zinc, copper, manganese and iron (Oudeh et al., 2002; Rout and Das, 2003). On the other hand, some metals that are nonessential to the body can be toxic even in a small amount, such as cadmium and lead (see Table 1-1) (Tuzen, 2003). Metals occur in different amounts in nature, and can be found in water, soil, and flora. They come from the weathering of the soil and rocks in the earth's crust.

Table 1- 1 National Recommended Water Quality Criteria, (SEPA, 2006)

Metals	Fresh water Acute µg/L	Fresh water Chronic µg/L
Arsenic	340	150
Cadmium	2	0.25
Chromium (III)	570	74
Lead	65	2.5
Mercury	1.4	0.77
Nickel	470	52
Zinc	120	120

1.1.1 Sources of metals

Chemical, physical and biological weathering can release elements from rock. The rates are controlled by various factors such as temperature and pH (Alloway, 1990; Dill et al., 2001; Galloway et al., 1982; Lantzy and Mackenzie, 1979). The natural sources such as atmospheric deposition of airborne particles come from volcanic activity, wind erosion, forest fire smoke, and oceanic spray. Metals are also released because of human activities, such as manufacturing processes and fossil fuel combustion. The natural sources and sources from human activities are shown in (Figure 1-1).

Around 7000 BC, humans performed copper smelting and the environmental impacts of metallurgy were felt in many parts around the world in prehistoric times. In the times before the industrial revolution, the rate of metal production from anthropogenic sources was relatively low (Tylecote et al., 1983). The industrial revolution increased the amounts of metals such as lead, copper, and zinc in the environment from anthropogenic sources. Between 1850 and 1990, production of these metals increased nearly 10-fold, with emissions increasing in parallel due to the high demand for metals (Nriagu, 1996). The industrial revolution changed from wood as a source of fuel to coal, and the impact of coal mining, refining and combustion processes introduced considerable amounts of metal emissions to the environment. Table 1-2 shows golobal emissions of trace elements to the atmosphere in 1983, and estimates of subsequent inputs to water and soil. Table 1-3 shows global mean metal concentrations in the air and soil and river sediment. The comparison between table 2 and 3 indicated the significant reductions in metal concentrations, which may be due to advances in pollution control technology, the regulations and reductions in use in the combustion of gasoline.

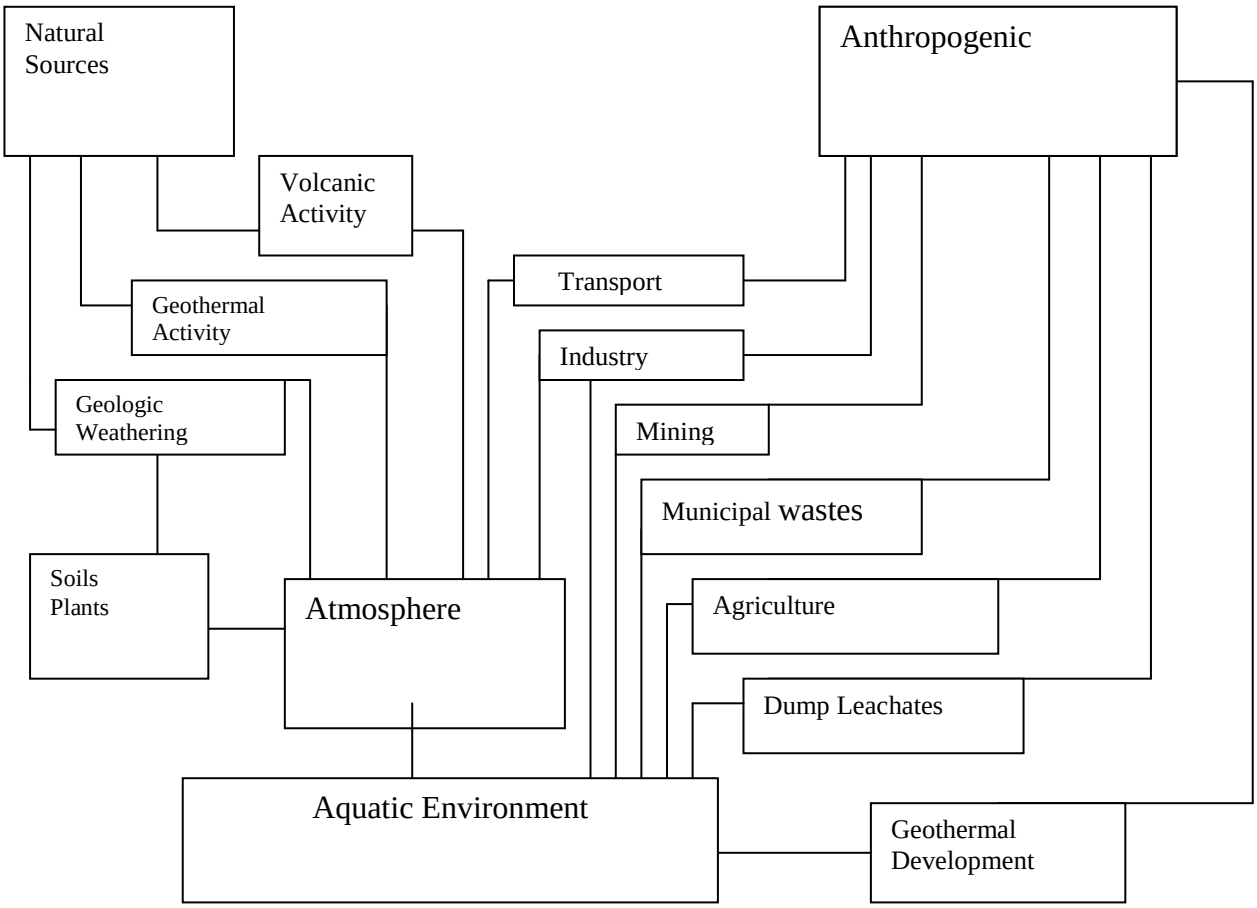

Figure 1-1 Natural and Anthropogenic sources of the heavy metals (Foster and Charleworth, 1996)

Table 1- 2 Globale Emission of trace metals into the atmosphere, water and soils (in 1000 metric tonnes per year) (From Nriagu and Pacyna, 1988).

Metals	Air		Water		Soil	
	Range	median	Range	median	Range	median
As	12-25	19	12-70	41	52-112	82
Cd	3-12	7.6	2.1-17	9.4	5.6-38	22
Cr	7-53	30	45-239	142	484-1309	896
Cu	19-50	35	35-90	112	541-1367	954
Hg	0.9-6	3.6	0.3-8.8	4.6	1.6-15	8.3
Mn	10-65	38	109-414	262	706-2633	1670
Mo	0.8-5	3.3	1.8-21	11	30-145	88
Ni	24-87	56	33-194	113	106-544	325
Pb	288-376	332	97-180	138	479-1113	796
Sb	1.5-5.5	3.5	3.9-33	18	4.7-47	26
Se	1.8-5.7	3.8	10-72	41	6-76	41
V	30-142	86	2.1-21	12	43-222	132
Zn	70-194	132	77-375	226	689-2054	1372

Table 1- 3 Global mean metal concentrations (µg/g) in the air and soil and river sediment (Rauch and Pacyna, 2009).

Metals	Atmosphere	soil	River (sediment)
Cu	0.0000008	39	100
Zn	0.000002	48	250
Fe	0.0004	33000	48000
Pb	0.000001	27	35
Ag	0.00000002	2.6	0.07
Ni	0.0000005	25	90
Cr	0.0000009	130	100
Al	0.0006	62000	89000

1.1.2 Metals in the air

The air is an important medium of transport for metals that are usually present in the atmosphere as aerosol particles. Table 1-4 shows that concentrations vary markedly from one region to another and from metal to metal. The aerosol particles have different sizes, ranging from 5 nm to 20 µm, but the majority of particles are between 0.1 and 10 µm in diameter. Humans and animals can both inhale these aerosols. In addition, the greatest environmental impact in the long term is during deposition under gravity or washout on to plants, lakes, soil, rivers and sea. The aerosols can be classed into two main forms: primary aerosols are directly spread into the air from the earth's surface and secondary aerosols are formed by chemical reactions in the atmosphere (Alloway, 1990; Bradl, 2005).

Table 1-4 Concentrations of selected elements in air at various locations (ng/m^3). From Alloway (1990), quoting from Bowen (1979).

Metals	South Pole	Europe Median (range)	North America Median (range)	Volcanoes (Hawaii /Etna)
Ag	<0.0004	1(0.2-7)	1(<0.04-2.4)	30
As	0.007	16(1.5-53)	15(1.7-40)	5.5-850
Au	.00004	(0.0001-0.006)	(<0.003-0.3)	8
Cd	<0.015	(0.5-620)	(<1-41)	8-92
Co	0.0005	(0.2-37)	3(0.13-23)	4.5-27
Cr	0.005	25(1-140)	60(1-300)	45-67
Cu	0.036	340(8-4900)	280(5-1100)	200-3000
Hg	-	(<0.009-2.8)	(0.007-38)	18-250
Mn	0.01	43(9-210)	150(6-900)	55-1300
Mo	-	(<0.2-3.2)	(<1-10)	-
Ni	-	25(4-120)	90(<1-120)	330
Pb	0.63	120(55-340)	2700(45-13000)	28-1200
Sb	0.0008	8(0.6-32)	12(0.08-55)	45
Se	0.0056	3(0.15-800)	5(0.06-30)	9-21000
Sn	-	(1.5-800)	(<10-70)	-
Ti	-	0.06	0.22	-
U	-	0.02	<0.5	-
W	0.0015	0.7(0.35-1.5)	4(0.03-6)	-
Zn	0.03	1200(13-16000)	500(<10-1700)	1000

1.1.3 Metals in soil

The natural sources of metal in the environment are from rocks and soils. Primary minerals occur in igneous rocks (these crystallize from molten magma). Table 1-5 shows the average contents of metals in some selected rocks. In addition, anthropogenic contamination increases the amounts of metals in the soil. Table 1-6 shows the range of toxic metals in the soil and the range of concentrations of metals in agricultural soils, under normal agricultural practices. In England and Wales, the Environment Agency has estimated that there are around 10000 contaminated sites covering 300,000 ha; while in Scotland there are 67,000 sites, covering 82,000 ha. The total number of metal contaminated sites in Europe is about 300,000 (Environment Agency, 2004; SEPA, 2009; USEPA, 2001).

Table 1-5 The natural average contents of metals mg/kg in selected rocks (from Bradl (2005)).

Metals	Granite	Basalt	Shale	Limestone	Streams mg/l
Al %	7.2	8.2	8.0	0.42	50
Cd	0.13	0.21	0.3	0.3	0.01
Co	4	47	20	0.1	0.1
Cr	10	185	100	11	1
Cu	20	94	50	4	7
Fe %	1.42	8.6	5.1	0.38	40
Hg(ppb)	0.03	0.09	0.4	0.04	0.07
Mn %	0.045	0.18	0.09	0.11	7
Mo	1	1.5	2.627	3	0.6
Ni	10	145	60	20	0.3
Pb	17	7	20	9	1
Zn	50	118	85	20	20

Table 1-6 Typical concentrations of some trace metals in soils from Bohn et al., (1985); Kabata-Pendias and Pendias (1992).

Element	Normal range in soil (total) µg/g dry wt	Concentration (total) µg/g dry wt in soil
Cr	5-1000	75-100
Mn	200-2000	1500-3000
Co	1-70	25-30
Ni	10-1000	100
Cu	2-100	60-125
Zn	10-300	70-400
Cd	0.01-7	3-8
Sn	<5	50
Hg	0.02-0.2	0.3-5
Pb	2-200	10-400

1.1.4 Metals in water

The metals available in the surface water may be due to water flow in the soil and rock, such as limestone ($CaCO_3$) and granite (quartz, mica and feldspars). This effect of water on rocks influences the solubility of the metals and affects the mobility of metals in the river system. Metals can be adsorbed onto clay minerals, Fe and Mn oxy-hydroxides and organic matter in the streams, rivers, springs, ponds and lakes or absorbed onto living systems such as algae. Furthermore, metals can be introduced by agricultural and industrial activity, land filling, mining, and transportation into rivers (Alloway, 1990; Bradl, 2005).

1.1.5 Metals in river systems

Trace elements occur in different river environments: the water body, suspended matter, bed sediments, and organisms (Ongley et al., 1982). Most of the metals' load is held and distributed by suspended particulate matter in river system environments (Coveli et al., 2007). Several earlier studies suggest that suspended particles can play an important role in carrying metals in the river system (Giesy and Briese, 1977; Reuter and Perdue, 1977; Hoffmann et al., 1981; Salbu et al., 1985; Tanizaki et al., 1992; Dai and Martin, 1995; Ross and Sherrell, 1999, Hill and Aplin, 2001). Some metals such as aluminium and iron, which are the main elements in rocks, therefore occur as trace elements in the natural water system. The concentration of the trace elements is lower than 1 mg/l in natural waters

(Alloway, 1990; Bradl, 2005). Table 1-7 shows the average concentration of some major and trace metals in the suspended sediment of the world's rivers.

Many factors can affect levels of trace elements in rivers, such as their relative abundance in the continental crust and their mobility during weathering and transport (Alloway, 1990). The nature of the suspended materials, such as clay, iron oxide and organic matter, affects the adsorption of metals and the availability of dissolved metals in the river systems. The existence of trace elements in water does not necessarily mean they come from rocks, because volumes of waste materials come from human activity (Miller, 1997). Some factors such as geology, weathering and the effects of manufacturing and agricultural production can affect natural waters (Pehlivan, 2010). A mixture of factors such as soil, flora, water cycle, and element controls the availability of metals in the fluvial system (Jain and Sharma, 2001; Zhang and Huang, 1993; Aurada, 1983; Warren, 1981).

Table 1-7 Average concentrations of some major and trace elements in the suspended sediments of the world rivers (Viers et al., 2008)

Metals	Unit	South America	North America	Russia	China	Africa	Europe
Na	%	0.4	0.5	1	0.4	0.3	0.7
Ca	%	1.5	2.2	2.6	1.1	2.2	6.3
Mg	%	0.5	1.1	1.7	1.1	0.9	1.3
K	%	1.7	1.8	1.9	2.5	0.9	1.8
Fe	%	5.29	4.5	7.88	4.6	7.5	4.3
Mn	µg/g	700	1430	5767	970	1478	1884
Zn	µg/g	184	137	300	145	130	346
Co	µg/g	16	15	30	21	23	16
Cr	µg/g	79	115	260	117	130	164
Ni	µg/g	46	50	123	68	78	66
Pb	µg/g	76	22	35	64	46	71

1.2 The nature of suspended particles in rivers

1.2.1 The origin of suspended particles

Rivers and streams carry a mixture of suspended sediment arising from different locations and different source types. The geology of the area in the river systems affects the particle characteristics of the suspended sediment. The parent materials also influence the particle size of the suspended sediment (Walling and Morehead, 1989). The physicochemical and biological characteristics of river systems can affect the loading within and between rivers depending on contact time and location of the sediment (Droppo and Jaskot, 1995). Clay sediment plays a very important role in suspended sediment concentration of watercourses and lakes (Walling and Morehead, 1989). In addition, the nature of the soil controls the composition and physical and geochemical properties of the suspended sediment in the river. The suspended particulate matter typically contains quartz, clay and other silicate minerals and hydrous metal oxides, as well as organic particles such as microorganisms, diatoms and plant detritus (Hillier, 2001).

Soil erosion by water and wind sources is responsible for much of the suspended sediment, which comes from soil processes such as break up and dispersal of the soil particles (Miller, 1931; Bennett, 1955; Foth, 1990). Water erosion is the result of rainfall and surface runoff, which affects the soil and causes a change in characteristics such as chemical, physical and biological, and reduces the fertility of the soil (Pimentel et al., 1995; Lal, 2000, 2006; Morgan, 2005; Zachar, 1982). Soil erosion is affected by soil type, topography, climate, and land use management (Bennett, 1939; Zachar, 1982; Morgan, 2005). Human activities can affect erosion through the removal of vegetation and changing the discharge regulations (Salant et al., 2008). Some factors such as slope gradient, length of slope, and size and shape of the watershed, have an effect on the erosion. High slope gradient increases the velocity of flowing water, which allows the transfer of additional material from the soil (Hillel, 2004).

Runoff is defined as part of the rainfall that does not infiltrate or accumulate on the soil surface but moves to the bottom of the slope. Flow occurs only when rainfall intensity exceeds soil infiltration rate, the duration and rate of rainfall impact the runoff and erosion. Fertilizer and nutrients are transported from the vegetation area, pasture or meadow as sediment by the runoff to the rivers (Hillel, 2004). Plant growth reduces the transport capacity for the flow of sediments by decreasing runoff amounts by reducing the stream average speed (Molina et al., 2009).

Agricultural land is the most vulnerable to erosion because of poor vegetation cover and seasonal disturbance of the soil surface (Stavi and Lal, 2001). Cultivated land left fallow with no vegetative cover is particularly vulnerable to runoff and erosion. Erosion can occur from various land use conditions on the areas of agricultural and grazing lands and forest areas. Increased soil erosion comes from the conversion of natural forests or grasslands to agricultural land. On croplands, the greatest erosion potential occurs with high intensity rainfall and minimum residue cover. Runoff and erosion are usually high in the land left fallow with no vegetative cover. The excessive grazing can reduce the vegetation cover, which may increase the soil erosion potential by both water and wind and maintain the vegetation on the surface of the forest, reducing loss of soil.

1.2.2 Physical characteristics of the suspended particles

The specific surface area of the sediment, which has a major control on its surface chemistry, increases markedly with decreasing particle size. The reason for the suspended sediment having a high surface area is because most of the particles are of clay and colloidal dimensions. This gives suspended sediment an important role in influencing the transport of metals. The chemical and physical properties of different constituents of the suspended materials, such as ion exchange capacity and specific surface area, differ. Decreased grain size increases the amount of the contaminant and nutrient concentration because the fine particles have a larger surface area for contaminant adsorption (Radakovitch et al., 2008). Bentonite has more metal adsorption capability than kaolinite. Other factors can affect the cation exchange capacity of the clay and suspended materials such as the mineralogy, surface area and crystallinity. Metals link easily to clay materials because the chemical and physical properties of the clay materials confer a high ion exchange capacity (Boenigk et al., 2005).

1.2.2.1 Kaolinite

Kaolinite is one of the main types of phyllosilicate clay in the soil. Kaolinite is white in colour with a small negative charge. Kaolinite has a low level of isomorphous substitution. The chemical structure is one tetrahedral silica sheet and one octahedral alumina sheet; it is of a 1:1 layer type mineral (see figure 1-2). The replacement of Si^{4+} by Al^{3+} in the silica tetrahedral sheet causes this negative charge, also of Al^{3+} by Fe^{2+} and Mg^{2+} in the octahedral sheet (White, 2006). There is strong hydrogen bonding between the oxygen atoms and hydroxyl groups of adjacent lattice layers. Kaolinite has a low surface area (5-100 m^2/g) (Sposito, 1989; Bohn et al., 1985).

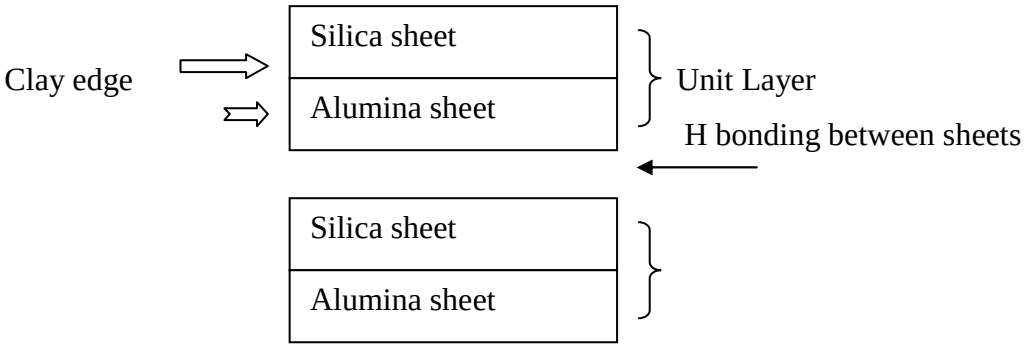

Figure 1- 2 The kaolinite structure (White, 2006)

1.2.2.2 Bentonite

Bentonite has a low degree of isomorphous substitution. Bentonite is related to clay minerals of the smectite group, which are characterized by a large surface area per unit of weight (700 to 800 m^2/g). The chemical structure consists of two tetrahedral silica sheets and one octahedral alumina sheet: this is type 2:1 (see figure 1-3). Bentonite is an expanding clay due to entry of cations and water molecules into interlameller spaces (Sposito, 1989; Bohn et al., 1985).

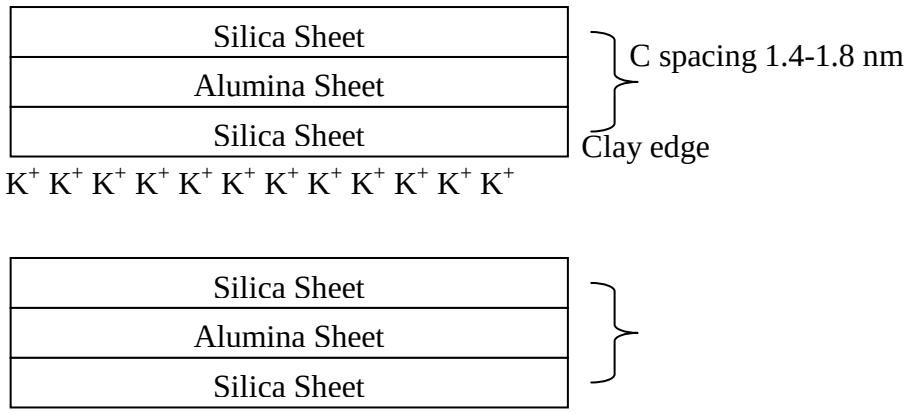

Figure 1-3 The bentonite structure (White, 2006)

1.2.2.3 Hydous Oxides

Hydous oxides are secondary minerals that form when Fe, Al and Mn are released from primary minerals by weathering. There are several iron oxides, such as hematite (-Fe_2O_3), goethite (FeOOH) and ferrihydrite ($Fe_2O_3.H_2O$). Iron oxides exist in the soil in different colours: red, yellow and brown. Isomorphic substitution of Al for Fe in goethite is common, especially in highly weathered soils (Sposito, 1989; Bohn et al., 1985).

1.2.2.4 Humic materials

Humic materials are substances that come from humus in the soil, created through microbial activity decomposing organic matter. There are two decomposable types of humic materials in the environment; the first one is easily decomposable in the environment such as phenolate and carboxylate compounds, and the second is resistant decomposable in the environment such as lignin (Sposito, 1989; Bohn et al., 1985).

1.2.3 Particle transport in rivers

Some factors such as river flow; slope gradient and length; particle size, and erosion and deposition affect suspended particle transport and deposits in the riverbed. Two types of suspended sediment can be transported in the rivers, coarser sediment with high flow condition and fine sediment with low flow condition. Figure 1-4 shows the distribution of mineral and organic colloids as a function of size in aquatic systems. Two main fractions can be identified in the suspended sediment systems. The particulate fraction (diameter > 0.2 µm) usually quickly settles to the bed sediments and the colloidal fraction (diameter < 0.2 µm) remains suspended longer and may facilitate the transport of adsorbed species over appreciable distances (Bio et al., 2002; Buffle and Leppard, 1995). The particle size in the water column can affect the surface area, settling velocity, and the deposition rate of the suspended sediment (Horowitz and Elrick, 1987).

River discharge is different from one season to another, which can affect the mobility and concentration of the metals (Foster and Charlesworth, 1996). Metals are transported in a fluvial system in dissolved form and adsorbed to the surface coating of the suspended particulate matter (Bibbly and Webster-Brown, 2006). River flow plays an essential role in metal transport (Walling and Morehead 1989). Fine material can control the metal transport more than large particles and is suitable for transporting metals at low river flow. In addition, a larger volume of water carrying a large amount of the sediment causes an increase in the total metal load. Sometimes under low flow conditions of the river system, there is a large amount of metals compared with load in high flow conditions (Gallo et al., 2006).

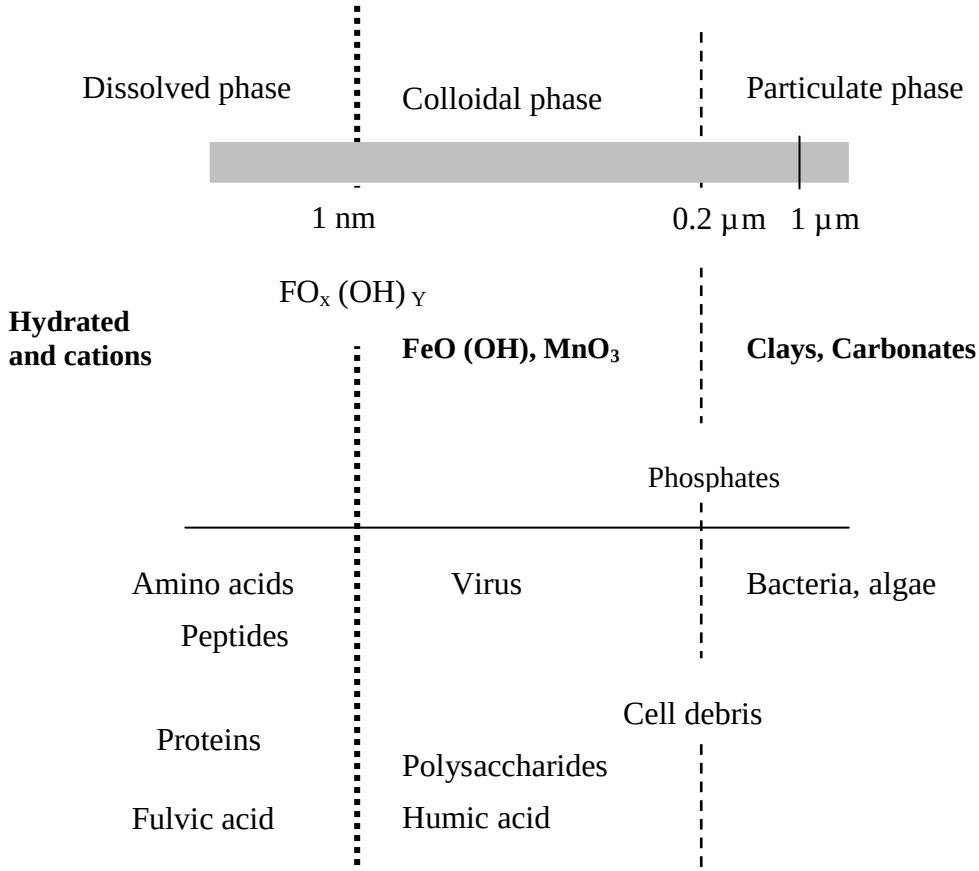

Figure 1-4 Distribution of mineral and organic colloids as a function of size in aquatic systems (Buffle and Leppard, 1995).

1.3 The role of suspended particles in the transport of metals

1.3.1 Metals in suspended sediment

In different riverine environments, there are a number of chemical and physical procedures (erosion, transport, and coagulation) that affect the shape and size of suspended particle matter (Droppo and Jaskot, 1995). Metals in the suspended sediment come from many sources and paths. Hatje et al., 2003 has argued that there are many compounds in particles that have a variety of surface chemical properties and affect metal adsorption characteristics. Some factors such as the type of weather, river basin, the origin of the sediment and transfer processes can affect the nutrient and contaminant content of the sediment (Walling and Morehead, 1989). The particulate phase in the fluvial system route is the most important transporter of metals in the geochemical cycle (Gibbs, 1977; Martin and Meybeck, 1979). Metals move between the water and suspended particles by adsorption and desorption routes (Salomons and Forstner, 1984; Foster and Charlesworth, 1996). In the river, three phases of metals can be identified, the suspended particulate phase, bed load phase and dissolved phase (Droppo and Jaskot, 1995). Table 1-8 shows the different average concentration of major and trace elements in the suspended sediment of the world's rivers.

Table 1-8 The average concentrations of major and trace elements in the suspended sediment of the World Rivers (Viers et al., 2008; Savenko, 2007; Martin and Meybeck, 1979).

Metals	Unit	Suspended sediment average concentration	Standard Deviation (σ)	Martin and Meybeck	Savenko
Ca	%	2.59	2.80	2.15	2.60
Fe	%	5.81	4.81	4.8	5.03
K	%	1.69	1.04	2	2.15
Mg	%	1.26	1.40	1.18	1.44
Na	%	0.71	0.93	0.71	0.82
Mn	µg/g	1679	5011	1050	1150
Zn	µg/g	208	237	250	130

1.4 Environmetal chemistry of metals studied

In the current study, different metals were determined in different chapters. In chapter four Cu, Pb and Zn were measured to determine the distribution between solid and solution phases of different materials. While in chapter five samples were analyzed for Ca, Fe, K, Mg, Mn and Zn, based on some of the monthly data obtained from Kelvin river tributaries during a 2009 and 2010 sampling period. In chapter five Cu and Pb were not determined, because the concentrations measured in the first two months of sampling period were lower than the detection limit.

1.4.1 Calcium

Calcium is an essential component for animals and plants. Calcium has atomic number 20. Calcium abundance in the water naturally comes from availability of Calcium in the earth's crust. The weathering is the main source of Calcium. Calcium exists naturally in water; it may dissolve from rocks such as limestone, marble, calcite, dolomite, gypsum, fluorite and apatite. Calcium can then be stored as a cation (a positively charged ion) on soil exchange sites (negatively charged). Calcium is an important determinant of water hardness. Calcium causes hardness of water, because it can be found in water as Ca^{2+} ions. In water solution, calcium is mainly present as Ca^{2+}, but it may also occur as $CaOH^{+}$, or as $CaSO_4$ in seawater. Various compounds of Calcium such as $Ca(NO)_3$ are applied as fertilizer. Calcium maintains healthy bones and teeth. Calcium reacts with water, according to the following reaction mechanism.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

This reaction forms calcium hydroxide that dissolves in water as a soda, and hydrogen gas. Under normal conditions calcium carbonate is water insoluble. When carbon dioxide is present carbonic acid is formed, affecting calcium compounds (Emsley, 2003; Faust and Aly, 1983; Greenwood and Earnshaw, 2002; Mason, 2002; Ramade, 1987; Wright, 2003).

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2\,HCO_3^{-} \longrightarrow Ca(HCO_3)_2$$

1.4.2 Copper

Copper is an essential element for plants and animals; Table 1-9 shows the average concentrations of copper in some components of the environment. Copper has an atomic number of 29. The average concentration of Cu in the Lithosphere is 70 mg/kg. The main minerals are found as impurities include chalcopyrite ($CuFeS_2$) and oxide cuprite (Cu_2O) and tenorite (CuO). In soil at a normal range of pH the Cu $(H_2O)_6^{2+}$ ion predominates in aqueous solution and can form very stable complexes with humified organic matter. Copper in plant function is a part of the group of redox enzyme systems (oxidases). Copper is generally used in the manufacture of wire and electrical equipment. The range of copper in an adult is about 100-150 mg. The ability of the human body to excrete copper is poor (Bradl, 2005; Alloway, 1990).

Table 1-9 Common value of copper concentration mg/kg in the environment (Bradl, 2005)

Material	Average concentration	Range
Igneous rocks	125	80-200
Sandstone	30	6-46
Limestone	6	0.6-13
Shale and clay	35	23-67
Coal	17	1-49
Fly ash	185	45-1452
Sewage sludges	690	100-1000
Soils	30	2-250
Freshwaters (μg/l)	3	0.2-30

1.4.3 Iron

Iron is one of the metals available on the surface of the earth. Iron has atomic number 26. Iron is released into the water environment by weathering processes. The major minerals occurring are magnetite, hematite and goethite. Naturally occurring iron oxide and iron hydroxide are water insoluble. The water solubility of some iron compounds increases at lower pH values. Dissolved iron is mainly available under acidic conditions and neutral. There is a difference between water soluble Fe^{2+} compounds and generally water insoluble Fe^{3+} compounds. Water solubility increases when these are reduced to Fe^{2+} under reduction reactions. In soil saturated with water, iron is converted to Fe^{2+} iron, thus enabling plant iron uptake. Iron is a dietary requirement for most organisms, and plays an important role

in natural processes as Fe^{2+}. Oxidized tertiary iron cannot be applied by organisms freely, except at very low pH values (Emsley, 2003; Faust and Aly, 1983; Greenwood and Earnshaw, 2002; Mason, 2002; Ramade, 1987; Wright, 2003).

1.4.4 Lead

Lead has been an important metal in civilization for thousands of years. Table 1-10 shows values of lead concentration in components of the environment. Lead has atomic number 82. The solubility and mobility of the lead compounds are low, but the accumulation in the soil comes from microbial degradation. Lead does not react with water under normal conditions. In the availability of oxygen and water metallic lead is converted to lead hydroxide. In the environmental chemistry of the elements, Pb is dominated by Pb^{2+} ions in the soil solution, which can be sorbed on to secondary Fe and Mn oxides, alkaline earth carbonates, the soil humus and silicate lattices. Lead was used in pipes to supply water and was put in cosmetics, and is still used for pigments for paint and in battery making. It is used a lot in the metal industry, and, until recently, was also used in the petrol industry (Lower and Maurice, 1998). Paints, pesticide production, lead smelting and refining, lead acid battery breaking, fumes from car exhausts, and sewage sludge are the sources of lead in the environment. Long-term exposure to high levels of lead can cause nervous disorders (Bradl et al., 2005; Alloway, 1990).

$$2Pb + O_2 + 2H_2O \longrightarrow 2\ Pb(OH)_2$$

Table 1-10 Common values for lead concentration mg/kg in the environment (Bradl, 2005)

Material	Average concentration	Range
Igneous rocks	15	2-30
Sandstone	7	1-31
Limestone	9	-
Shale and clay	20	16-50
Coal	16	Up to 60
Fly ash	170	21-220
Sewage sludges	1832	136-7627
Soils	-	2-300
Freshwaters (μg/l)	3	0.06-120

1.4.5 Magnesium

Magnesium is one of the most abundant elements available in the earth's crust. Magnesium has atomic number 12. Magnesium is not found free in nature, but available in a large number of minerals such as dolomite (calcium magnesium carbonate; $CaMg(CO_3)_2$) and magnesite (magnesium carbonate; $MgCO_3$). Magnesium is a determinant of water hardness; usually magnesium compounds are removed from the water, because of the role magnesium plays in the hardness of the water. Magnesium is essential for plant and animal nutrition. Magnesium is mainly present as Mg^{2+}, and $Mg(OH)_2$ in water solutions (Emsley, 2003; Faust and Aly, 1983; Greenwood and Earnshaw, 2002; Mason, 2002; Ramade, 1987; Wright, 2003).

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

1.4.6 Manganese

Manganese is one of the most common metals in the soil, where it occurs as oxides and hydroxides. Manganese has atomic number 25. The major natural atmospheric sources of manganese are ocean spray, forest fires, vegetation, and volcanic activity. The main sources of manganese from the anthropogenic environment are from discharge of municipal wastewater and sewage sludge, mining, and processing mineral resources, and emissions from steel, alloy also the production of iron and the burning of fossil fuels. The pH and redox potential are the two major variables to determine manganese solubility in the soils. Manganese exists in the aquatic environment in two main forms (MnO_2) and (Mn_3O_4). In aerobic conditions the Mn (IV) oxidation state is the most stable, but in reducing conditions the Mn (II) state is favoured. The manganese oxides are the natural result of the oxidation of Mn (II) or reduction of manganese Mn (IV) (Bradl et al., 2005; Alloway, 1990).

1.4.7 Potassium

Potassium is a necessary constituent for the growth of plants. Potassium has atomic number 19. The main source of potassium in the soil solution is the weathering of parent rock. Potassium is not found free in nature. Potassium occurs in various minerals, from which it may be dissolved through weathering processes. Examples are feldspars (orthoclase and microcline), which are however not very significant for potassium compounds production, and chlorine minerals carnalite and sylvite. Potassium reacts

rapidly and intensely with water, forming a colourless basic potassium hydroxide solution and hydrogen gas, according to the following reaction mechanism:

$2K + 2H_2O \rightarrow 2KOH + H_2$

In water this element is mainly present as K^+ ions. A number of potassium compounds are used in synthetic fertilizers, especially potassium nitrate (Emsley, 2003; Faust and Aly, 1983; Greenwood and Earnshaw, 2002; Mason, 2002; Ramade, 1987; Wright, 2003).

1.4.8 Zinc

Zinc has atomic number 30. The composition of rock can control the zinc in the soil. There are many sources of zinc from natural and human activity, giving about 50 mg/kg as the average concentration of zinc in most soils (see table 1-11). The amount of zinc present in acid rocks is about 40 mg/kg, and in basaltic rocks, about 100 mg/kg. The solubility of zinc depends on the temperature and pH in the water and increases with increasing acidity. The source of Zn pollution in the air comes from the burning of coal, other fossil fuels and metal smelting. Zn can contaminate plants, due to the accumulation of Zn from sewage sludge on agricultural land (McGrath et al., 2000). Zinc does not react with water molecules; Zinc reacts with H^+ ions and after that can react with the water (Emsley, 2003; Faust and Aly, 1983; Greenwood and Earnshaw, 2002; Mason, 2002; Ramade, 1987; Wright, 2003).

Table 1- 11 Common values for zinc concentration mg/kg in the environment (Bradl, 2005)

Material	Average concentration	Range
Igneous rocks	65	5-1070
Sandstone	30	5-170
Limestone	20	<1-180
Shale	97	15-1500
Fly ash	449	27-2880
Sewage sludges	2250	1000-10000
Solis	50	1-900
Freshwaters (μg/l)	15	<1-100

1.5 Sampling and analysis of suspended aquatic particles

1.5.1 Water sampling methods

Water samples are typically collected from rivers using different methods such as grabbing in a sampling bottle at different depths below the surface, usually ranging from 0.2 to 1 m. In addition, other methods use pump systems, such as a diaphragm pump (Pettine et al., 1994; Van Berkel and Beckett, 1996). The types usually used are the peristaltic pump (Sigg et al., 2000; Wen et al., 1999) or plastic or submersible bilge pumps. After this stage, the samples are moved to the laboratory and processes occurring during transport can often cause problems. For example, it can cause particle aggregation and redistribution of the metals between the solution and particle phases. That is because there are changes in speciation when transferring the sample from its natural environment to a laboratory where all the treatments are performed. Samples are stored at low temperatures and in the dark, and preservatives are added to try to reduce these changes in the water sample. In some research the water is filtered directly at the river during the sampling procedure (Hill and Aplin, 2001; Wen et al., 1999; Benoti and Rozan, 1999).

1.5.2 Collection and concentration of suspended sediment

Suspended particles are typically collected from the river sample by using a range of filter paper sizes. Some use 0.45 μm pore size filter paper to remove large particles (Pettine et al., 1994; Garnier et al., 1996; Tipping et al., 1997), and others use 0.2 μm-pore size to collect the fine particulate and natural organism cells. Others use molecular filters with nominal cut offs between 1 to 30 kDa to differentiate between dissolved and insoluble metals in river water.

Many problems with filtration can be distinguished. In some cases the pore sizes are not correct, and there are important losses in the sample, which come from the change in pore size and blockage as the sediment particles combine. In addition, with the pump pressures that can be obtained, it is difficult to filter more than a hundred millilitres of the water sample by normal filtration. Moreover, Pettine et al. (1994) and Garnier et al. (1996) found that an increase in the concentration of the suspended particles caused a decrease in the percentage of the metals in the filtrate.

1.5.3 Tangential flow filtration

Tangential flow filtration is a technique used to separate and purify biomolecules. It can be used in a wide range of vital areas such as immunology, chemistry and microbiology. Tangential flow filtration is easy technique to set up and use, fast and efficient in short time, and economical (Horowitz et al., 1989a; Conato et al., 2003).

1.5.4 Centrifugation

Centrifugation is a method used to separate suspended particles from water samples. The separation can be done in the laboratory or even in the field (Sigg et al., 2000). Centrifugation is a quick technique used to separate and purify bio molecules. The centrifugal force causes the particles to move radially away from the axis of rotation, when a suspension is rotated at a certain speed. Molecules or cells in a liquid suspension will eventually settle at the bottom of a container due to gravity; the centrifugal force applied is 500 times greater than the Earth's gravitational force. The main problem is the amount of sample that can be processed by centrifugation. The centrifuge speed, time and collection depth in the tube control the specific particle size.

1.5.5 Continuous flow centrifugation

Continuous flow centrifugation uses large volumes of the water sample. After the water sample is pumped from the river, the sample is processed directly. From the Humber and Tweed basins (UK) Walling et al. (2000) tried to recover sediment by using continuous flow centrifugation from the river sample. Tangential flow filtration equipment can be used only in the laboratory, while the filtration and continuous flow centrifugation can be used in the field and in the laboratory (Sigg et al., 2000; Ran et al., 2000).

1.6 Methods for particulate fraction collection and metals analysis

1.6.1 Analytical techniques

Many analytical methods are used to determine the metals in suspended sediment samples. Table 1-11 shows the different methodologies for collecting samples from the river, the fractionation techniques, size ranges utilized, and analytical methods for elemental composition determination. Spectroscopic techniques are the most common methods, such as UV-visible spectrophotometry, flame photometry, atomic absorption spectrometry, and inductively coupled plasma atomic emission spectrometry. In addition, there are micro-analytical techniques, which can determine the spatial distribution of metals in a sample, like micro X- ray absorption analysis. Different research studies use different methods, including three multi-element analytical techniques that appear well suited for multi-element analysis of inorganic trace concentrations; inductively coupled plasma atomic emission spectrometry (ICP-AES); inductively coupled plasma mass spectrometry (ICP-MS); and instrumental neutron activation analysis (INAA) (Bounouira et al., 2008).

Table 1-12 Fractionation techniques, size ranges utilized and analytical methods for elemental composition determination (Conato et al., 2003)

Fraction methods	Fraction sizes	Analytical methods	System
Cascade filtration	0.45 µm 1.2 µm	ICP-MS	Different rivers (Switzerland
Filtration (lab)	0.45 µm	ICP-AES and	Italy, Morocco,
Filtration (lab)	0.4 µm	ETAAS	Poland, Po (Italy)
Filtration (lab)	0.4 µm	AAS	Po (Italy)
Centrifugation (lab)		GFAAS and FAAS	Po (Italy)
		ICP-MS	Po (Italy)
SPLITT(split-flow thin) cell fractionation	0.2-1-1.6-4.2 µm 0.2-25 µm	ETAAS	Trent (UK) Ouse (UK)
Tangential flow filtration	25 µm		
Filtration (lab)	0.2-1.5 µm		
SPLITT cell fractionation	0.2-25 µm	ICP-AES	Po (Italy)
Tangential flow filtration	25 µm		
Filtration (lab)	<1 kDa		
Cross flow filtration (lab)	1kDa-0.1 µm 0.1-0.45 µm 0.45 µm	GFAAS and ICP-MS	Seven rivers in NE England and SW Scotland
Filtration (in situ)	<10 kDa		
Cross flow ultra Filtration (lab)	10 kDa-0.45 µm 0.45-1µm	ICP-MS and	Thur
Membrane filtration (in situ)	1-10 kDa	GFAAS	(Switzerland)
Continuous-flow centrifugation (in situ)	0.45 µm 0.003-0.006-0.2-1µm		
Cross flow ultrfiltration (lab)		GFAAS	
Filtration (in situ)	<0.4 µm		Galveston Bay
Tangential flow filtration	1-25 µm	ICP-AES	(Gulf of Mexico)
SdFFF	25 µm	flame AAS	Namoi (Australia)
Continuous-flow centrifugation	0.4 µm 0.4 µm	FDC(fast distribution coefficient)	
Filtration (lab)			Lena Estuary
Filtration (lab)	Upper cut off: 0.8 µm	AAS	(Russia)
Filtration (lab)			LOIS river database, Humber system (UK)
SdFFF (sedimentation field-flow fractionation)	(GFAAS),1 µm(ICP-MS)	GFAAS and ICP-MS	Po (Italy)
Tangential flow filtration	0.2-25µm 25 µm		
Filtration (lab)	1 kDa		
Cascade ultrfiltration on membranes (Samples spiked with radioisotopes)	100 kDa 0.45 µm 0.025 µm 0.1 µm	γ-ray spectrometry	Vienne (tributary of river Loire, France)
Multistage Tangential flow membrane fractionation (lab)	0.45 µm 1 µm	ICP-AES and ICP-MS	Weisse Elster and Mulde (Germany)

1.6.2 Flame atomic absorption spectrometry

Atomic absorption spectrometry is a commonly used and reliable analytical technique for the detection of certain elements. Atomic absorption spectrometry is easy to use, but can only measure one element at a time. The principle of the AAS instrument is explained below:

The sample solution is aspirated into a flame in order to generate the element in its atomic form. Light from a hollow cathode lamp is passed through the flame and the atoms absorb the light (atomic absorption) and enter an excited state. The hollow cathode lamp contains the element to be measured. During the atomic absorption there is a reduction in the intensity of the light beam, which can be measured, and the decrease is directly correlated with the concentration of the elemental atomic species. Measurements are carried out comparing light absorbance of the unknown sample with the light absorbance of the known calibration standard. The wavelength of an absorbed line is identical to the wavelength of the line that is emitted when the electron returns from the excited state to the ground state. Every elementary particle has a unique set of energy states. When an atom absorbs light, the energy of the atom increases, because the absorbed light excites electrons from a ground state to higher level of energy; after a short period the excited species relaxes, transferring its excess energy to other atoms in the medium.

1.6.2.1 The hollow cathode lamp

The hollow cathode is encased in a glass tube, which is filled with either argon or neon, which is ionised by a high current applied between the anode and cathode. This ionisation causes high energy positive ions to be formed, which move to the cathode surface, causing sputtering and excitation of the atoms contained on it. When these excited atoms return to their ground state, they emit a sharp line spectrum that is characteristic of the element to be analysed, which is then directed through the silica window at the end of the lamp and is the incident beam on the flame. It is important that emission lines from the gas filling the tube do not coincide with those of the element being measured. The hollow cathode lamp generates the analytical lines for the element of concern, giving a constant yet intense light of these analytical lines.

1.6.2.2 The nebulizer

The sample solution is aspirated through a plastic tube into the nebulizer, the purpose of which is to convert the sample solution into a fine aerosol mist. The fine mist of sample solution droplets, with diameters from <5 to 25 µm, then passes into the spray chamber. Sample droplets of the correct diameter are selected by spray chamber (large drops broken or trapped) and the mist is mixed with the oxidant and fuel gases. The nebulizer delivers the liquid sample at a controlled rate, as a fine aerosol into the flame.

1.6.2.3 The flame

The purpose of the flame is to act as an energy source to decompose the sample being analysed into its constituent atoms. When the sample solution mist passes into the flame, the solvent quickly evaporates to give solid particles, which melt and vaporise. The vapour then decomposes into the constituent atoms of the sample, which can then absorb photons of light from the hollow cathode lamp to become excited. So, in order to achieve maximum sensitivity, the sample should be completely atomised, without excitation or ionisation so that the flame generates atoms of the element of interest, because the excited or ionized atom does not absorb the most intense wavelengths corresponding to ground-state atoms.

1.6.2.4 The monochromator

Because the hollow cathode lamp emits only narrow spectral lines, it effectively performs the monochromation and the monochromator is required only to select the wavelength at which the absorbance is to be measured, and to reject any other lines. The monochromator isolates analytical line photons passing through the flame, and discards scattered light of other wavelengths from the flame.

1.6.2.5 The photomultiplier tube

The detector used in flame instruments is most commonly a photomultiplier tube. Photomultiplier tubes are able to measure wavelengths in the range of 193.7 nm to 852.1 nm. When a photon from the monochromator strikes the surface of the photomultiplier tube an electron is emitted, converting the light signal from the monochromator into an electrical signal. After amplification, by using a data handling system, transmitting the result to a computer, the absorbance value is shown on a readout device, which is nowadays most commonly a digital display.

1.7 Research aim and objectives

1.7.1 Aims

The work of this study was carried out to investigate the role of suspended sediment to transfer of metals in tributaries of the River Kelvin.

1.7.2 Objective

1. To assess the ability of sediment components (single and mixed) to take up heavy metals in the laboratory and study the distribution of the Cu, Pb and Zn between solid phase and solution phase.

2. To evaluate the analytical procedure for investigation of the role of fine suspended sediment in the transfer of metals in River Kelvin tributaries.

Chapter 2

Materials and Methods

This chapter describes the materials, the sampling location, sampling procedures and the analytical methods that were common to all the experiments.

2.1 Filtration procedures

2.1.1 Routine methods

All the glassware and plastic ware used during the research was cleaned in a 2-5% solution of Decon 90 chemical cleaner, and rinsed 3 times with de-ionised water before being dried overnight in an oven.

2.1.2 Filter papers

Some method development for selection of the filter paper was done, as described in Chapter 3. Different types of filter paper were used. The filter papers were used not all from the same box. As a result, two Whatman filter papers, 47 mm diameter, 1.2 μm pore-size micro-fibre filters (Acid Treated low Metal) and 90 mm diameter 0.2 μm pore size Nylon membrane filters, were used in the current research. The filter papers were weighed before being used for filtering of water samples, and after filtering to determine the mass of particles collected. (See Chapter 3 for filter paper procedures).

2.1.3 Pump

The samples were filtered with a pump (Buchi Vac. V-511, figure 2-2) in order to make the filtration processes quicker, as filtration without the pump takes more than a week for filtration of five litres of water sample through a 0.2 μm pore size filter.

2.1.4 Reagents

Deionised water was taken from the ELGA (model LA613) distillation system.

Figure 2-1 Pump Buchi Vac. V-511, used for prepareation of the sample.

2.2 Digestion procedures

2.2.1 Aqua regia digestion for pseudo total metal concentration

The pseudo total heavy metal concentration was measured using aqua regia digestion. This procedure is widely used for heavy metal determinations in environmental samples and is suitable for determining metal concentration in most samples even at low concentration. Aqua regia was prepared by mixing; three parts 50% 6M HCl to one part 69% HNO_3 (Rauret et al., 1999).

The filter papers were weighed before and after the filtration process to determine the weight of suspended particles collected. Filters bearing collected particles were then placed in a 50 ml beaker, 12 ml of aqua regia solution was added, and the beaker covered with a watch glass. The beaker was placed on a hot plate at a temperature of 115 ºC for 3 hours. The digestion was performed for 3 hour until all NO_2 was eliminated and the samples were clear. The digests were cooled and filtered with washing by distilled water. The digests were filtered by using a hardened filter paper (Whatman (54) Hardened 90 mm filter paper) into a 100 ml volumetric flask and made up to the mark with deionised water. A solution containing aqua regia only was used as a blank.

2.2.2 Preparation of AAS standards solutions

Fisher Scientific standard solutions of 1000 mg/l were used in all experiments. The standard solutions were nitrates of metals (Ca, Cu, Fe, Mn, Pb, and Zn) in 0.5 mg/l nitric acid as supplied. Pipettes were not inserted in the bottles at any time, to maintain the purity of the standard solution. Instead, a small volume of each standard solution was poured into a 50 ml beaker, from which 10 ml was measured with a bulb pipette into a 100 ml volumetric flask containing solvent (aqua regia), and made up to the mark with deionised water, to prepare 100 mg/l stock solutions.

In measuring total content of Ca, Cu, Fe, Mn, Pb, and Zn by FAAS, standard solutions for each metal were first prepared. FAAS is a suitable technique for this metal analysis because it has good sensitivity and a specific wavelength for the choose metals. Standard solution should give reading of about 0.2 absorbance units. The Pb standards had concentrations of 10 mg/l, 20 mg/l, 30 mg/l, 40 mg/l and 50 mg/l. Standard solution for Ca, Cu and Fe had concentrations of 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l and 5 mg/l. For Mg, Mn and Zn the concentrations were 0.5 mg/l, 1 mg/l, 1.5 mg/l, and 2 mg/l. The atomic absorption spectrometer was then calibrated with the standard solutions and the samples were analysed, checking the calibration after every 10 samples.

2.2.3 Measurement

Measuring the absorbance of one of the standard solutions prepared and varying the acetylene flow in the flame established the optimum fuel flow. A metal-free solution containing solvent only was used as a blank to zero the instrument. One of the standard solutions was used to reslope the instrument. A metal solution containing solvent only was used as a blank.

2.2.4 Measurement of the sample

The metal concentrations in the digests of the suspended particle samples were measured by using atomic absorption spectrometry. Metals in the water sample both before and after being filtered through 1.2 μm pore size filter and 0.2 μm pore size filter were also measured, between each reading; the instrument was zeroed with a metal-free solution containing solvent.

2.3 Measurement procedure

2.3.1 Atomic Absorption Spectrometry (AAS) Measurement

An atomic absorption spectrometer (Perkin Elmer 400 B model) was used in all the experiments. Operating parameters are shown in Table (2-1).

Table 2-1 Standard conditions employed for different metals analysis by atomic absorption spectrometry

Element	Wavelength (nm)	Lamp Current (mA)	Lamp Energy (Arbitrary units)	Flame Type	Fuel Flow (L /min)	Air Flow (L /min)	Top Standard mg/l	Detection limit mg/l
Ca	422.7	6	77	N_2O/ C_2H_2	7.5	7.5	5	0.107
Cu	324.75	30	80	Air/ C_2H_2	2.5	10	5	0.21
Fe	248.3	30	60	Air/ C_2H_2	2.5	10	5	0.022
Mg	285.2	6	73	N_2O/ C_2H_2	7.5	7.5	2	0.04
Mn	279.5	20	49	Air/ C_2H_2	2.5	10	2	0.016
Pb	283.3	15	65	Air/ C_2H_2	2.5	10	2	0.50
Zn	213.9	10	47	Air/ C_2H_2	2.5	10	2	0.057

2.3.2 Detection Limit (DL)

The detection limit is defined as the lowest concentration that can be clearly differentiated from the blank. The standard procedure for establishing detection limits by flame AAS is as follows;

A standard solution of known concentration of each element is prepared. In this study, the 1-5 mg/l Ca standard solution, 1-5 mg/l Fe standard solution, 0.5-2 mg/l Mg standard solution, 0.5-2 mg/l Mn standard solutions, and 0.5-2 mg/l Zn standard solutions were used. The instrument is calibrated with the range of standard solutions. Then using low concentrations of standard solution, ten readings are made with a blank between each standard reading. The standard deviation of each set of readings was noted. The mean and the standard deviation readings were used in the calculation for the detection limit as shown in the following;

Detection Limit (DL) = 3 x standard deviation (10 readings)/slope of calibration curve

2.3.3 Flame photometry

Potassium and sodium were determined by flame photometry, a form of flame emission spectroscopy. The flame photometer (Corning Model 410) was calibrated using 0-10 mg/l K standards or 0-10 mg/l Na standards by relevant dilutions of stock solutions. Using the standard graph for that particular metal, the emission value was converted to a concentration value.

The instrument was set for measuring either K or Na and the solution measured and the emission value noted.

A flame photometer consists of the following basic components:

1) The burner: a flame that can be maintained at a constant temperature and at a constant form.

2) Nebuliser and mixing chamber: a way of transferring a homogeneous solution into the flame at a stable rate. At a specific wavelength of light needed for quantitative analysis, the intensity of emitted light must be measured, usually the most intense wavelength emitted by the flame.

3) Interference filters: a means of isolating light of the wavelength to be measured from that of extraneous emissions.

4) Photo-detector: a way of determining the intensity of radiation emitted by the flame.

2.4 Sampling procedures and sampling and analyses

2.4.1 Sampling Methods – Field sampling

Water samples were taken for this research in an area to the north of Glasgow, Scotland, UK. Samples were taken from eight sites on tributaries of the River Kelvin. The River Kelvin rises about 55 meters above sea level near the village of Kelvinhead. Some tributaries of the main river are the Allander Water, Glazert Water, Luggie Burn and Bothlin Burn, see Figures from (2-3) to (2-13). The sites are listed in table 2-2.

2.4.2 River Catchment

The Allander water catchment is mainly in rural areas and developed mostly on basaltic materials. The main land use is upland grazing and there has been some reforestation and urban development (Milngavie) in the lower parts. The Glazert water catchment is overlain by mixed superficial deposits. Land use is mainly rough pasture in the upper catchment, with managed grassland and some forestry in the lower parts. There are a number of old mining villages in the Bothlin catchment, with significantly areas being urbanised, but also some pasture and forestry. The Luggie catchment is largely agricultural, with large urban development in the North (e.g. Cumbernauld), and some forests (SEPA, River Kelvin catchment monitoring Years; 2002-2005).

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Table 2-2 The sites used for sampling suspended sediment from the tributaries of the River Kelvin (Ordnance Survey, Glasgow & surrounding area map).

Sites number	Tributary name	Location (UK, Ordnance survey grid Reference)
1	Craigton Burn	NS 547757
2	Allander Water	NS 547758
3	Craigmaddie	NS 572743
4	Glazert Water	NS 628776
5	Bothlin Burn	NS 669734
6	Luggie Burn	NS 670735
7	Cameron Burn	NS 774725
8	Cameron Burn2	NS 778700

The samples were obtained using a plastic container to collect water from the river about two meters from the riverbank. The plastic bucket and sample bottles were rinsed with river water prior to sampling. Sample bottles were clearly labeled, and the water put in the plastic bottles onsite, before being returned to the university, and kept in the refrigerator in the laboratory.

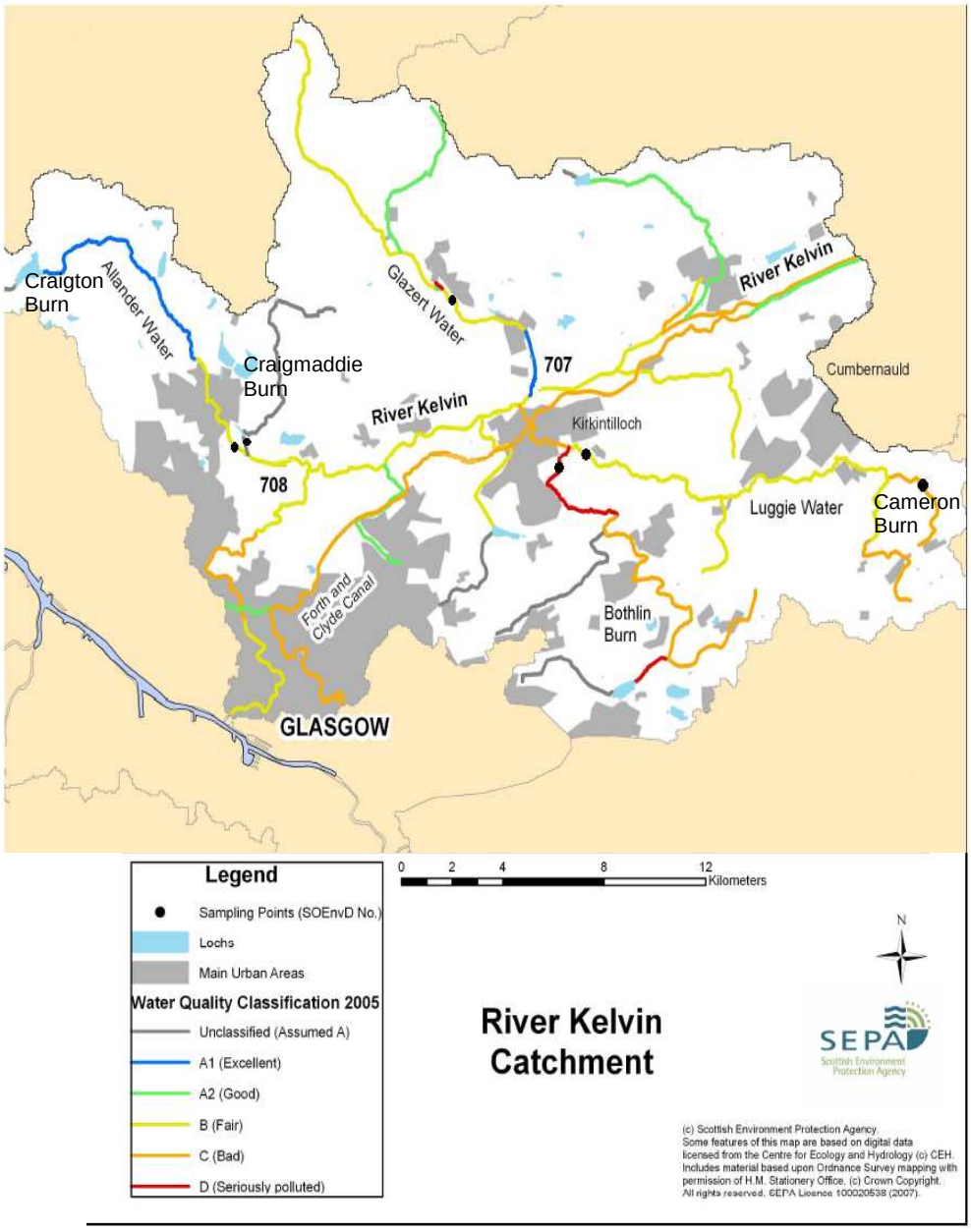

Figure 2-2 the tributaries of Kelvin River (SEPA, River Kelvin catchment monitoring Years; 2002-2005).

Figure 2-3 Craigton Burn, Allander water (Google-Image@2011 Infoterra Ltd and Blusky, GeoEye)

Figure 2- 4 Sampling site, left Craigton Burn, right Allander water.

Figure 2-5 Sampling site Craigmaddie Burn (Google-Image@2011 Infoterra Ltd and Blusky, GeoEye)

Figure 2-6 Sampling site Craigmaddie Burn

Figure 2- 7 Glazert water (Google-Image@2011 Infoterra Ltd and Blusky, GeoEye)

Figure 2- 8 Sampling site Glazert water

Figure 2-9 Luggie Burn (Google-Image@2011 Infoterra Ltd and Blusky, GeoEye)

Figure 2-10 Sampling site Luggie Burn

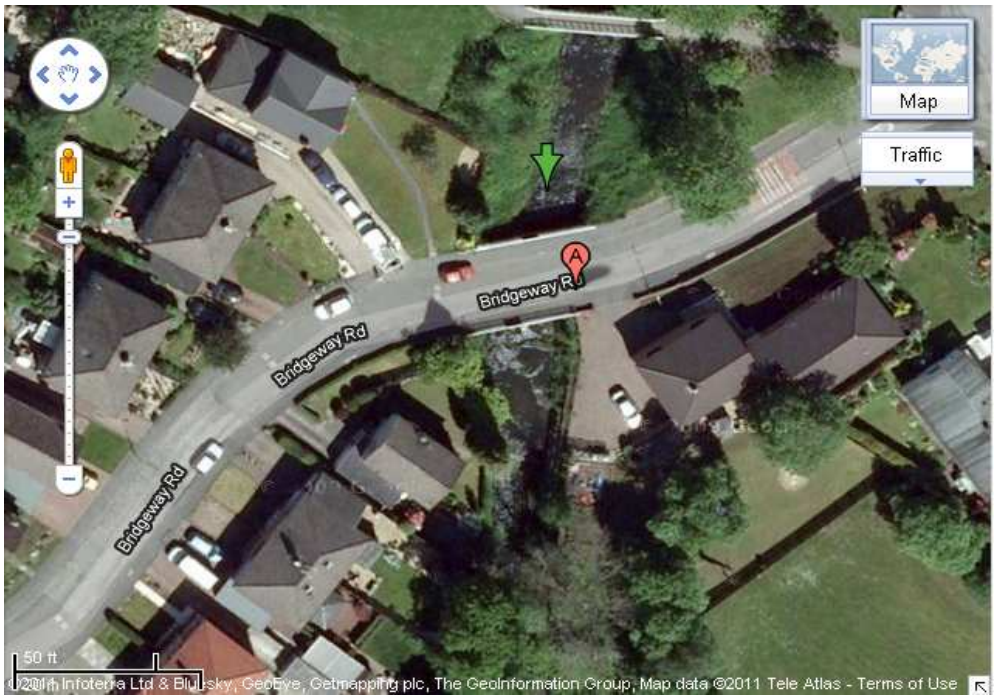

Figure 2-11 Bothlin Burn (Google-Image@2011 Infoterra Ltd and Blusky, GeoEye)

Figure 2- 12 Bothlin Burn sampling site

2.4.3 Sample collection

Six litres of water were taken at each sampling location at the dates shown in table 2.3. The two months gap in sampling collection was due to bad weather in December 2009 and January 2010.

Table 2-3 Dates on which sampling of the suspended sediment from the tributaries of the River Kelvin was conducted.

Number of Sampling month	Sampling time in 2009	Number of Sampling month	Sampling time in 2010
1	13th of June	9	10th of February
2	14th of July	11	24th of March
3	15 th of August	12	5th of May
4	14th of September	13	8th of June
6	16thof November		

2.4.4 Preparing the sample

The river samples were subjected to a two-step filtration process. The sample was first passed through a 47 mm diameter, 1.2 μm pore-size micro-fibre filter (Acid Treated low Metal), and second through a 90 mm diameter, 0.2 μm pore-size nylon membrane filter. A motorized vacuum pump was used to assist the filtration process.

2.4.5 Filtration using 47 mm diameter, 1.2 μm pore-size micro-fibre filters (acid treated low metal)

The filter paper of 1.2 μm pore size, 47 mm diameter was weighed before use. Five litres of the sample were then passed through it to collect the suspended particles. After filtration the filter paper was removed from the filter support using tweezers, placed on a clean, dry watch glass and dried overnight in air in a covered place. The mass of the filter paper with

residue particles was then determined and the difference in mass between this value and the original weight was calculated.

2.4.6 Filtration using 90 mm diameter, 0.2 μm pore-size nylon membrane filter

Five litres of the sample were filtered through a 0.2 μm pore size (90 mm diameter) nylon membrane filter, after a 1.2 μm pore size, 47 mm diameter glass micro fibre (acid treated low metal) filtration, to collect the suspended particles in the size range 1.2 μm -0.2 μm The filter paper with 0.2 μm pore size was weighed before and after use.

After filtration the filter paper was removed from the filter support using tweezers, placed on a clean, dry watch glass and dried overnight in air in a covered place. The mass of the filter paper with residue particles was then determined and the difference in mass between this value and the original weight was calculated.

2.5 Laboratory studies using defined sediment components

Typical components of aquatic suspended materials were studied in the laboratory to assess their ability to take up heavy metals. These materials were, kaolinite, and bentonite, from British Drug Houses, laboratory chemicals division Poole, England, also iron oxide material (Goethite synthesized in house), and humic acid (obtained from Sigma-Aldrich Chemie GmbH, Riedstr, Germany).

The Goethite was prepared by (Blanc-Lapierre, 2008) following the procedure:-

1. Solution of iron oxide (III) nitrate Nona-hydrate 100 ml of 1 M prepared using distilled water was added to a polythene screw bottle.
2. Sodium hydroxide 180 ml of a 5 M solution was added with stirring.
3. Diluted the solution to 500 ml with distilled water and put in an oven at 70° C for about sixty hours. During this time, large amount of red-brown ferrihydrite suspension is supposed to transform into a compact yellow solution of goethite.
4. The solution was filtered by using a hardened Whatman 50 filter paper and rinsed 4 times with de-ionised water before being dried overnight at 70° C in an oven.
5. The sample was ground to produce a fine powder.

2.5.1 Studies of individual components

The experiment was performed by adding different weights (0.0 g, 0.3 g, 0.5 g, 0.8 g and 1 g) of one of the materials (kaolinite, bentonite, iron oxide or organic matter) to one litre of distilled water containing trace metal at 1 mg/l concentration of metal in a clean, dry glass beaker. The individual steps were as follows:

1. Approximately e.g. 0.0, 0.3, 0.5, 0.8 and 1 g of dry material was weighed in a beaker. A metal solution containing aqua regia was used as a blank.
2. 1 ml of 1 g/l concentration of metal was added to one litre of distilled water.
3. The 0.3 g of the material was added to the 1 mg/l concentration solution. A stirrer bar was added and the beaker placed on a magnetic stirrer for mixing the sample.
4. The sample was mixed for times ranging between 15 and 30 minutes.
5. Sample material was filtered through pre weighed 0.2 μm pore size filters and the filter paper was dried and reweighed to determine the mass of material recovered.
6. The filter paper was digested using aqua regia, and the metal associated with the test material was measured by FAAS, between each reading, the instrument was zeroed with a metal-free solution containing aqua regia.

2.5.2 Studies of mixed systems

Further experiments were performed in order to assess take up of metal by mixtures of components listed above. These material were mixed is the proportions as shown in table (2-4).

Table 2-4 Examples of the mixed material weights.

kaolinite+ bentonite	kaolinite + iron oxide	kaolinite + humic acid
0.2 g-0.8 g	0.2 g-0.8 g	0.2 g-0.8 g
0.5-0.5 g	0.5-0.5 g	0.5-0.5 g
0.8 g-0.2 g	0.8 g-0.2 g	0.8 g-0.2 g

1) Approximately e.g. (0.2 g - 0.8 g, 0.5 g - 0.5 g and 0.8 g - 0.2 g) of dry material was weighed in a beaker.
2) 1 ml of 1 g/l concentration of metal was added to the one litre of distilled water.
3) The mixed material was added to the 1 mg/l concentration solution. A stirrer bar was added and the beaker placed on a magnetic stirrer for mixing the sample.
4) The sample was mixed for times ranging between 15 and 30 minutes.
5) Sample material was filtered through the weighted 0.2 μm pore size filters and the filter paper was reweighed to determine the mass of material recovered.
6) The filter paper was digested using aqua regia, and the metal associated with the test material was measured by FAAS; between each reading, the instrument was zeroed with a metal-free solution containing solvent.

Chapter 3

Selection of filter papers for collection of suspended aquatic particles

3.1 Introduction

This chapter describes the initial work performed using membrane filter papers to collect suspended materials from river water. This was carried out in order to select the most appropriate filter type for use in subsequent experiments. Membrane filters have come into general use in recent years for the filtration of water samples prior to analysis. Membranes are screen filters that remove suspended materials from the water in different size ranges. Filtration is widely accepted as a way of producing an acceptable sample and filtration has become a first step in the preparation of water samples for trace metal analysis. Often, the filtrate is analyzed to study 'dissolved' metal concentration. However, in this work, the filter is used to collect suspended particles for trace metal analysis.

Some research studies have investigated possible contaminants associated with a range of filter types, and the adsorption capacity of filter papers (Dams et al., 1972; Habib and Minski 1981; Jardine et al., 1986; Walsh et al., 1988). Other research studies have been concerned with the physical effects of filtration, and have emphasized differences in trace metal concentrations that are likely to be measured if filters of different pore size are used (Liu et al., 1977; Bertsch, 1989). Berg and Royset (1993) found that, in different brands of filter paper, there are different concentrations of trace metals; for example, glass fibre filters had considerable concentrations of metals such as Cr, and Zn. In addition, the quartz filter type showed measurable concentrations of elements including: B, Cr, Mg, Mo, Na, and Zn. Marvin et al. (1970) found that several types of filter paper are contaminated with Cu. Robertson (1965) and Spencer and Manheim (1969) have determined that the heavy element content of membrane filters used in the filtration process of water samples is a potential source of contamination. Some studies have found that some of the factors associated with filtration can considerably change heavy metal concentrations: such as: filter type, filter diameter, filtration method (Horowitz et al., 1992). Filter paper may be adsorbing some metal from the solution phase or may be releasing metals causing contamination of the solution (Hedberg et al., 2011). In the current work, probable contaminants associated with a range of filter paper products were measured to try to develop methods for removing them prior to use. Initially the study entailed a comparison of filter types, using glass micro fibre and nylon membrane of different diameter size (47, 90, 125 mm) of various pore sizes (1.2 μm and 0.2 μm).

3.2 47 mm diameter, 1.2 μm pore-size micro-fibre filters

Filters were analyzed both before and following washing with 5 L of deionised water.

3.2.1 Digestion and measurement

Three replicates of filter paper from the same box were digested in 3:1 hydrochloric acid /nitric acid solution, an aqua regia digest (see section 2.2.1). Measurements of metals in the aqua regia digest of 1.2 μm pore size micro fiber filters (47 mm) were done by FAAS. A metal solution containing solvent only was used as a blank. Table 3-1 shows the concentrations of various heavy metals found in these filters, before, and after 5 liters deionised water was filtered through.

Table 3-1 The concentrations of metals (mg/g) in 1.2 μm pore size, 47 mm diameter, micro fibre filter papers, with and without washing by 5 L deionised water (n=3) (n=number of the replicates).

Filter paper 1.2 μm	Concentration mg/g			
	Fe	K	Na	Zn
No washing	0.147- 0.20	4.1- 4.7	12-13	5.57- 5.76
5L deionised water	0.145- 0.20	2.0-2.38	5.1-5.5	2.50- 2.60

The results indicate that the filter paper was contaminated with metals and that levels of contamination were variable. The concentrations generally decreased after 5 liters of deionised water was passed through the filter paper except for Fe but, even so, the concentrations were measurable and unacceptable for use to determine metal concentrations in suspended sediments.

There are in fact two features that make the filter paper of 47 mm diameter, 1.2 μm pore-size not appropriate to use to assess heavy metals in the suspended materials. These are the small diameter size, which affects the time of the filtration, and the high concentrations of some heavy metals. It is possible that using another filter paper with a larger diameter may reduce the filtration time.

3.3 125 mm diameter, 1.2 μm pore-size micro-fibre filters

The same procedures that are described in section 3.2 were carried out here with the larger filters. The filter papers used came from the same box.

3.3.1 Digestion and measurement

The filter paper was digested in aqua regia 3:1 hydrochloric acid /nitric acid solution, (see Section 2.2.1). Concentrations of metals were measurable by AAS in the aqua regia digests of 1.2 μm micro fibre filters (125 mm) diameter. A solution containing solvent only was used as a blank. Table (3-2) shows concentrations of a number of metals before and after filtering through 5 litres of deionised water and after the filter papers had been left in the air to dry in a drawer.

Table 3-2 The metal concentrations (mg/g) in 1.2 μm pore size, 125 mm diameter, micro fibre filter paper, with and without washing by 5 L deionised water (n=3) (n=number of the replicates).

Filter paper 1.2 μm	Concentration mg/g			
	Fe	K	Na	Zn
No washing	0.075- 0.079	3- 3.7	12.5- 13.3	5.1- 5.5
5 L deionised water	0.04- 0.043	1.8- 2	4.5-5.9	2.4-2.63

Larger diameter of the filter paper makes the filtration process faster, and reduced the filtration time taken. On the other hand, there were high contamination levels in the filter papers that make their use not appropriate. There is no different contamination level between 125 mm and 47 mm 1.2 μm pore size micro-fibre filters with different size of the filter areas. Application of an acid pre treatment could possibly remove the contamination from the filters. Therefore this was performed.

3.3.2 Acid treatment of 125 mm diameter, 1.2 μm pore-size micro-fibre filters

The filter papers were washed by 100 ml of different concentrations of HNO_3 passing through the filter paper, to try to remove the contamination of heavy metals in the filter paper.

3.3.2.1 Washing single filter paper by 100 ml of different concentrations of HNO_3

The 125 mm diameter, 1.2 μm pore-size micro-fibre filters were washed using 100 ml of different concentrations of HNO_3**.** The concentrations were 0.1 M, 1 M and 5 M HNO_3. The acid was filtered through different filter papers, and a different paper was used for each acid wash concentration.

3.3.2.2 Digestion and measurement

The filter paper was digested in 3:1 hydrochloric acid /nitric acid solution, an aqua regia digest (see Section 2.2.1). A metal solution containing solvent only was used as a blank. Measurements of metals in the aqua regia digest of 1.2 μm micro fibre filters (125 mm) diameter were done by AAS. Table (3-3) shows the concentrations of metals in the filter paper digests.

Table 3-3 Concentrations of Fe and Zn (mg/g) in 125 mm diameter, 1.2 μm pore-size micro-fibre filters washed separately by 100 ml HNO_3

HNO_3	Concentration of Fe mg/l	Concentration of Zn mg/g
0.1M HNO_3	0.020	0.65
1M HNO_3	0.19	0.34
5M HNO_3	0.023	0.47

After washing the filter paper by different concentration of HNO_3 acid, the result showed some change in the metal concentrations, compared with those that had 5 litres deionised water passed through these filter. However the concentration is still unacceptable for both Zn and Fe in the filter paper. The measurements were made for iron and zinc only, because these metals are important in the next phase of the research. Another method for acidic treatment of the filter paper may be able to help to remove the contamination in the filter paper digest, washing a filter sequentially with several concentrations of acid.

3.3.2.3 Washing the filter paper with different concentrations of 100 ml HNO_3 sequentially

This method applies 100 ml of HNO_3 0.1 M, 1 M and 5 M acid concentration washing to the same filter paper, not like the previous method, which applied acid washing to different filter papers. 125 mm diameter, 1.2 μm pore-size micro-fibre filters was washed sequentially in different concentration of HNO_3 0.1 M, 1 M and 5 M.

3.3.2.4 Digestion and measurement

The filter paper was digested in 3:1 hydrochloric acid /nitric acid solution, an aqua regia digest (see Section 2.2.1). Measurements of metals in the aqua regia digest of 1.2 μm micro fibre filters (125 mm) diameter were done by AAS. A metal solution containing solvent only was used as a blank. Table (3-4) shows measurable concentrations of some heavy metals in the filter paper digest. Even when each filter was washed in sequence by

different concentrations of 100 ml HNO_3 (0.1 M, 1 M and 5 M) the results show considerable concentration of zinc in the filter paper.

Table 3-4 The metal concentrations (mg/g) in 1.2 μm pore size, 125 mm diameter, micro-fibre filters after being washed by 100 ml HNO_3 sequentially with different concentration of (0.1, 1 and 5M of HNO_3)

Number of replicate	Concentration Fe mg/g	Concentration Zn mg/g
1	0.02	0.72
2	0.02	0.62
3	0.06	0.62
4	0.06	0.45

In the experiment of single acid washing, there were some decreases in the metal concentrations compared with concentrations measured after washing in 5 liters deionised water. The results with sequentially acid washing show the metal concentrations are still high and unacceptable. In addition, the sequential acid washing increased the Fe concentration. The overall results of the various washing treatments indicated that contamination could not be eliminated or reduced to an acceptable level with washing. The next step was to test commercially available acid washed filters.

3.4 47 mm diameter, 1.2 μm pore-size micro-fibre filters (Acid Treated low Metal)

A new filter paper was used and analysed to check the amounts of contamination present, Whatman 1.2 μm pore size micro fibre filters (47 mm) diameter (Acid Treated low Metal). Three replicates of 1.2 μm pore size micro fibre filter paper were washed though with 5 litres deionised water, and left in the air to dry.

3.4.1 Digestion and measurement

The filter paper was digested in 3:1 hydrochloric acid /nitric acid solution, an aqua regia digest (see Section 2.2.1). Measurements of metals in the aqua regia digests of 1.2 μm micro fibre filters (47 mm) diameter (Acid Treated low Metal) were by AAS. A metal solution containing solvent only was used as a blank. Concentrations of various heavy metals after washing with 5 litres of deionised water are shown in table (3-5).

Table 3-5 The metal concentrations (mg/g) found in 1.2 μm pore size, 47 mm diameter, in three replicates micro fibre filter paper (Acid Treated low Metal) with and without washing by deionised water (n=3) (n=number of the replicates).

Filter paper1.2 μm	Concentration mg/g					
	Ca	Fe	K	Mg	Na	Zn
No washing	2.9- 3.1	0.043-0.05	4.1-4.4	1.07-1.11	7.4-7.9	0.011-0.012
5 Litres deionised water	2.8- 3.8	0.039-0.04	2.9-3.4	0.95-0.99	6.3-7.1	0.010-0.010

The results show there was no marked change in the contamination amount after the washing by 5 litres of deionised water. In contrast to the other filters tested, the 1.2 μm micro fibre filters (47 mm) (Acid Treated low Metal) had a low concentration of Zn. The Fe concentration in Acid Treated low Metal filter paper is higher than previous filter papers used.

In spite of the small diameter of the 1.2 μm micro fibre filters (47 mm) (Acid Treated low Metal) that adversely affects the time of the filtration, this brand was selected because it has low concentration of Zn. On the other hand, the presence of varying amounts of other metals in the 1.2 μm pore-size micro fibre filter apparently cannot be eliminated or reduced. Use of this filter paper will therefore require results to be blank corrected for the concentrations of elements already present (Ca, Fe, K, Mg, and Na), by subtracting the contaminated concentration, measured in the digested filter paper, from the total concentration measured in the digested suspended sediment from river sample. In this

subtraction, the average metal concentration in the filter paper was used, because each filter paper shows different concentrations of the metals.

3.5 47 mm diameter 0.2 µm pore size Membrane Filters Nylon

Analysed filter material 0.2 µm pore size (Membrane Filters Nylon 47 mm) shows that there is no contamination detectable. On the other hand, the filtration process takes a long time; using small diameter size (47 mm) caused a long filtration time. A larger diameter size could possibly help to make the filtration process faster.

3.6 90 mm diameter 0.2 µm pore size Nylon Membrane Filters

Analysis of the filter material 0.2 µm pore size membrane filters nylon (90 mm) shows that there is no metal contamination detectable by FAAS or FES. This filter paper was used in the all of the experiments in this study. The large diameter sizes (90 mm) help to make the filtration time to be shorter.

3.7 Discussion:

Analyses of digests of filter materials show that the 1.2 µm pore size micro fibre filter (47 mm diameter) had an unacceptable concentration of Zn, and a smaller concentration of Fe present. The metal concentration did not change when the filter papers were washed in 5 litres deionised water but remained unacceptably high as filters were digested along with sample. In addition, the small size of the filter paper (diameter 47 mm) lengthens the filtration time. All these things make this filter paper inappropriate to use to determine the metals in the suspended sediment from the river.

Using another size of filter paper (1.2 µm pore size micro fibre filter 125 mm diameter) makes the filtration quicker, and saves a lot of time compared with the 47 mm filter. But the results show that the concentration of some metals in this filter paper is similar to that of smaller filter. Even though the filtration time is shorter, the high contamination by metals makes this filter paper inappropriate to use to determine the metals in the suspended sediment from the river.

Treating the 1.2 µm pore size, 125 mm diameter filter paper, by using different methods of acid washing can possibly remove the metals in the filter paper. Specifically, washing the 125 mm diameter 1.2 µm pore size micro fibre filter with nitric acid can possibly take out the contamination of metals. Different concentrations of HNO_3 (0.1 M, 1 M and 5 M) were filtered through the filter paper, separately to remove the contamination. The results show that after filtering the acid through the filter paper, separately, there was still an unacceptable concentration of zinc.

Washing acid through the same filter paper in sequence did not show any change in the concentration of zinc and iron. Finally, the presence of varying amounts of metals in 125 mm diameter 1.2 µm pore-size micro fibre filter apparently cannot be eliminated or reduced by acid washing. All these effects make this filter paper inappropriate to use to determine the metals in the suspended sediment from the river.

Measurements on aqua regia digests of 1.2 µm micro fibre filters (47 mm) (Acid Treated low Metal) by AAS show that there was a low concentration of zinc before and after being washed through with 5 litres distilled water. In spite of the small diameter size, that affects the time of the filtration, and the high concentration of some major cations, this filter paper was acceptable in this study. This brand was selected because it has low concentrations of Zn and Fe. On the other hand, this filter paper does have high concentration of some major elements, and presence of varying amounts of metals cannot be eliminated or reduced. This filter paper was used in this research after correcting the concentration of the elements (Ca, Fe, K, Mg, and Na), by subtracting the contaminated concentration measured in the digested filter paper (contamination), from the total concentration measured in the digested suspended sediment from river sample. Unfortunately a larger diameter filter of this type is not commercially available.

Analysis of 0.2 µm pore size Membrane Filters Nylon 47 mm diameter filters shows that there is no contamination. On the other hand, the filtration process takes a long time; the large diameter size (90 mm diameter) 0.2 µm pore size causes the filtration time to be shorter.

3.8 Conclusion

In this study from the selection of filter papers for collection of suspended aquatic particles, 1.2 μm micro fibre filters (47 mm) (Acid Treated low Metal) were used to collect the larger diameter suspended sediment. The concentrations of the elements Ca, K, Mg, and Na were corrected, by subtracting the contaminated concentration, measured in the digested blank filter paper, from the total concentration measured in the digested suspended sediment from the river sample. In addition, 0.2 μm pore size membrane filters nylon 90 mm diameter was used to collect the fine suspended sediment between 1.2 μm and 0.2 μm.

Chapter 4

Laboratory studies using defined sediment components

4.1 Introduction

This chapter will evaluate the ability of different components of suspended fluvial material to take up heavy metals. Experiments were carried out to measure the distribution of copper, lead and zinc between an aqueous phase and solid phase sediment material. This study tries to simulate the natural system, exploring the sorption of trace metals on important materials, which are commonly found in the soil. The studies evaluate the heavy metal uptake in single sorption systems, and in a mixed system of clays, humic material and iron oxide.

The distribution coefficient, K_d, is the ratio of the concentrations of metal held on the solid phase to the concentration of the metal in solution: $K_d = [metal]_{solid} / [metal]_{solution}$

It represents the equilibrium that is achieved when metal ions in solution interact with sorption sites on the solid phase.

$$[metal]_{solid} \rightleftharpoons [metal]_{solution}$$

It does not however give any information about the mechanism of binding. K_d values have frequently been used to assess the relative concentration of metals in solution associated with suspended material (Yin et al, 2002). Use of K_d values has proven to be especially useful for assessing the ability of soil and sediments to immobilize contaminant heavy metals (Jalali and Moharrami, 2007) and radionuclides (Pulford et al., 1998; Standring et al., 2002). Materials representative of components of suspended particles were: kaolinite, bentonite, humic acid and iron oxide. Bentonite and kaolinite were from British Drug Houses, laboratory chemicals division Poole, England. The iron oxide material (Goethite) was synthesized in house and humic acid was obtained from Sigma-Aldrich Chemie GmbH, Riedstr, Germany. Copper, lead and zinc were chosen as representative of contaminant heavy metals. However it was not possible to measure Cu and Pb concentrations in the field study (Chapter Five) as they were below the limit of detection by AAS.

4.1.1 Heavy metal sorption behaviour of suspended kaolinite

The experiment was performed by adding different weights (0.3 g, 0.5 g, 0.8 g and 1 g) of the kaolinite to one litre of deionised water containing metal at a 1 mg/l concentration. The procedures are described in section 2.5.1.

4.1.1.1 Results and discussion

The results in table 4-1 give the recovery of kaolinite and distribution of Cu, Pb, and Zn between metals adsorbed on the solid phase and metal concentration in solution phase. The results show that most of the kaolinite was recovered on the filter paper. The majority of the metal was measured in the aqueous phase, with only a small amount measured in the solid phase. K_d values reflect distribution of metals between solid and solution phase.

Kaolinite is a one silica sheet: one alumina sheet clay mineral. The kaolinite tetrahedral sheet carries a small permanent negative charge due to isomorphous substitution of Si^{+4} by Al^{+3}, causing a single negative charge. The permanent charge is minor in kaolinite clay. The tetrahedral sites of kaolinite become permanently negatively charged and allow electrostatic interaction with positively charged ions. The kaolinite unit layers are held by hydrogen bonds between oxygen atoms on the tetrahedral face and hydroxyls on the octahedral face. That results in a low cation exchange capacity (CEC) (10-100 mmol/kg) and low specific surface area (10-20 10^3 m^2/kg) of kaolinite (Bohn et al., 1985). There are two distinct processes that have been proposed for the adsorption of heavy metals by kaolinite. The first is adsorption onto permanent negatively charged sites by electrostatic interaction with positively charged ions, and the second occurs on variable-charge groups at the edges of kaolinite crystals and these sites are generally more important than the permanent negatively charged sites (Schinder et al, 1987). The layer edges are primarily responsible for interaction of kaolinite with contaminant metals (Farrah et al., 1980).

Table 4-1 Recovery of kaolinite and distribution of Cu, Pb, and Zn metals between solid and solution phase.

A	B	C	D	E	F	G	K
Sample weight (g)	Weight of kaolinite recovered in filter paper (kg)	Recovery of kaolinite %	weight of metal in recovered kaolinite (mg)	Concentration of metal in kaolinite (mg/kg)	Concentration of metal in 1 L of filtered water (mg/l)	Recovery of metals (mg)	Kd (l/kg)
1mg/l Cu							
0.3	0.000299	99	0.075	251.3	0.9	0.908	279
0.5	0.000472	94	0.061	129.2	0.9	0.946	137
0.8	0.000785	98	0.112	142.7	0.8	0.841	172
1	0.000981	98	0.180	183.6	0.8	0.818	229
Average							**204**
1mg/l Pb						sd % =28	sd = 40
0.3	0.000294	98	0.109	368.7	0.8	0.868	430
0.5	0.000485	97	0.190	392.7	0.6	0.661	612
0.8	0.000775	97	0.219	282.5	0.6	0.625	468
1	0.000991	99	0.217	218.5	0.6	0.669	338
Average							**462**
1mg/l Zn						sd %= 31	sd = 63
0.3	0.000287	96	0.032	112.7	0.9	0.899	126
0.5	0.00047	94	0.070	149.5	0.8	0.852	177
0.8	0.000785	98	0.107	136.8	0.8	0.799	173
1	0.000964	96	0.077	79.8	0.8	0.879	92
Average							**142**
						sd % = 25	sd = 114

C= (B/A)*100,G=D+F, K= (E/F)

The affinity order of metal K_d for kaolinite was, Pb > Cu > Zn which was similar to previously reported results (Gu et al., 2008, Spark et al., 1995, Schinder et al., 1987, and Farrah and Pickering, 1976). In this study the pH values were not measured, because the parameters of the solution phase are fixed; low metal concentration and small material amount, which may not affect the pH. Previous studies such as Spark et al., 1995, Schinder et al., (1987) and Farrah and Pickering, (1976) have used a range of pH values to determine adsorption of metal on clay minerals. In general, the K_d value of Pb was slightly higher than those for the other metals tested. A number of aspects, including the accuracy of the analytical technique and the small adsorption capacities of the kaolinite can cause small changes in metal uptake (Farrah and Pickering, 1977).

4.1.2 Heavy metal sorption behaviour of suspended bentonite

The experiment was performed by adding different weights (0.3 g, 0.5 g, 0.8 g and 1 g) of the bentonite to one litre of deionised water containing metal at a 1 mg/l concentration. The procedures are described in section 2.5.1.

4.1.2.1 Results and discussion

Table 4-2 shows the recovery of bentonite and distribution of Cu, Pb, and Zn between solid and solution phases. The results show that most of the bentonite was recovered on the filter paper. The concentrations of Cu and Pb in solution following equilibration with bentonite were below the limit of detection for AAS, suggesting that most of the metal had been taken up on to the bentonite. It is therefore not possible to calculate K_d for these metals, but only to estimate a lower limit by using the limit of detection concentration (0.21 mg Cu/l and 0.5 mg Pb/l). K_d values for Zn could be calculated as the concentrations of Zn in solution was above the limit of detection. K_d values for Zn were high and this is probably because bentonite is a swelling clay, with a high surface area and a high cation exchange capacity. Metals can be adsorbed onto bentonite in the two distinct processes; on the permanent negatively charged sites, and on smaller variable charge sites, which occur on the edges of bentonite.

Bentonite has one octahedral sheet: two tetrahedral sheets. The bentonite has largely negative charges within the crystal, because of the extensive isomorphous substitution. The interlayer bonding is weak, which results in high cation exchange capacity (CEC) (800-1200 mmol/ kg) and high specific surface area (800×10^3 m^2/kg) (Bohn et al., 1985). Metal adsorption can occur as an ion exchange reaction at permanent-charge sites and formation of complexes with the surface hydroxyl groups. The amount of the surface layer charge plays an important role in determining the strength and type of bonding layers. On the other hand, the bonding is strong when the layer charge is negative, because cations go between the unit layers (Bohn et al., 1985).

Table 4-2 Recovery of bentonite and distribution of Cu, Pb, and Zn metals between solid and solution phase.

A	B	C	D	E	F	G	K
Sample weight (g)	Weight of bentonite recovered in filter paper (kg)	Recovery of bentonite (%)	weight of metal in recovered material (mg)	Concentration of metal in bentonite (mg/kg)	Concentration of metal in 1 L of filtered water (mg/l)	Recovery of metals (mg)	Kd (l/kg)
1mg/l Cu							
0.3	0.000285	94	0.97	3409	< 0.21	1.18	>16236
0.5	0.000462	92	0.99	2145	< 0.21	1.20	>10215
0.8	0.000608	76	0.58	953	< 0.21	0.80	> 4541
1	0.000923	92	0.75	812	< 0.21	0.96	> 3868
1mg/l Pb							
0.3	0.000277	92	0.59	2114	< 0.5	1.08	> 4228
0.5	0.000448	90	0.76	1694	< 0.5	1.25	> 3388
0.8	0.000745	93	0.69	915	< 0.5	1.18	> 1832
1	0.000977	92	0.73	754	< 0.5	1.23	> 1509
1mg/l Zn							
0.3	0.000277	92	0.58	2086	0.2	0.83	8347
0.5	0.000475	95	0.65	1363	0.2	0.88	5926
0.8	0.000793	99	0.78	980	0.2	1.04	3631

C= (B/A)*100, G=D+F K= (E/F)

4.1.3 Heavy metal sorption behaviour of suspended iron oxide (goethite)

The experiment was performed by adding different weights (0.3 g, 0.5 g, 0.8 g and 1 g) of the iron oxide (goethite) to one litre of deionised water containing metal at a 1 mg/l concentration. The procedures are described in section 2.5.1.

4.1.3.1 Results and discussion

Table 4-3 shows the recovery of iron oxide (goethite) and distribution of Cu, Pb, and Zn between solid and solution phases. The results show that most of the iron oxide (goethite) was recovered on the filter paper. Because most of the metals were measured in the solution phase and only small amounts were associated with the solid phase. Iron oxide has high surface area between 30-100 m^2/g (Ponthieu et al., 2006). Iron oxide (goethite) has a variable charge, which depends on the pH of the environment; the variable charge allows iron oxide (goethite) to interact with metals. The surface charge of the iron oxide (goethite) is positive under acidic conditions and negative under alkaline conditions. Iron oxide with net negative charge can bind or hold cations on their surface by ion exchange processes. Also iron oxide can bind or hold ions by ligand exchange process. In the current study the pH was unfortunately not measured and there is no explanation of how metals were associated with the solid phase. The results indicated that iron oxide (goethite) suspended sediment has low metal carrying ability, which may be because of the particular form of iron oxide used under the experimental conditions.

Table 4-3 Recovery of iron oxide and distribution of Cu, Pb, and Zn metals between solid and solution phase

A	B	C	D	E	F	G	K	
Sample weight (g)	Weight of bentonite recovered in filter paper (kg)	Recovery of bentonite (%)	weight of metal recovered material (mg)	Concentration of metal in bentonite materials (mg/kg)	Concentration of metal in 1 L of filtered water (mg/l)	Recovery of metals (mg)	Kd (l/kg)	
1mg/l Cu								
0.3	0.000277	92	0.019	68.5	0.98	1.00	70	
0.5	0.000448	89	0.021	46.9	0.99	1.01	47	
0.8	0.000752	93	0.023	30.6	0.95	0.97	32	
1	0.000972	97	0.028	28.8	1.01	1.04	29	
Average								**45**
1mg/l Pb						sd % =42	sd = 19	
0.3	0.000287	95	0.012	42.2	0.83	0.84	51	
0.5	0.00049	98	0.019	39.4	0.92	0.95	43	
0.8	0.000783	97	0.022	28.8	0.91	0.94	31	
1	0.000978	97	0.025	25.6	0.90	0.93	29	
								38
1mg/l Zn						sd % =26	sd= 10	
0.3	0.000284	94	0.009	31.7	0.82	0.82	39	
0.5	0.000489	97	0.005	10.2	0.86	0.87	12	
0.8	0.000736	91	0.007	9.51	0.72	0.72	13	
1	0.000976	97	0.008	9.23	1.04	1.05	9	
Average								**18**
						sd % =78	sd= 14	

C= (B/A)*100, G=D+F, K= (E/F)

4.1.4 Heavy metal sorption behaviour of suspended humic acid

The experiment was performed by adding different weights (0.3 g, 0.5 g, 0.8 g and 1 g) of the humic acid to one litre of deionised water, containing metal at a 1 mg/l concentration. The procedures are described in section 2.5.1.

4.1.4.1 Results and discussion

Table 4-4 shows the recovery of humic acid and distribution of Cu, Pb, and Zn between solid and solution phases. Humic acid is a major component of natural organic matter. Soil has about 70% content of organic materials such as carboxyl, phenolic hydroxyls and aromatic units. Humic acids are soluble under alkaline conditions, but are insoluble in acidic conditions (Kipton and Powell, 1992). It contains carboxyl, amine, hydroxyl and phenol functional groups. There are different compounds of humic material, such as fulvic acid and humic acid (Herrera Ramos and McBride 1996; Kretzschmar and Sticher 1997). The results show that the majority of humic acid was not recovered. That is because most humic acid materials passed through the filter paper to the solution phase. In this case it is not possible to derive K_d values, this because humic acid is largely in the solution phase. These results do not show the distribution of metal uptake, between solid and solution phases, because the majority of humic acid materials passed through the filter paper. On the other hand, humic acid materials passing through the filter paper to the solution phase this may be indicator of the high mobility process for metals associated with the humic acid in the solution.

Table 4-4 Recovery of humic acid and distribution of Cu, Pb, and Zn metals between solid and solution phase.

A	B	C	D	E	F	G
Sample weight (g)	Weight of humic acid recovered in filter paper (kg)	Recovery of humic acid %	weight of metal in recovered material (mg)	Concentration of metal in humic acid (mg/kg)	Concentration of metal in 1 L of filtered water (mg/l)	Recovery of metals (mg)
1mg/l Cu						
0.3	8.53E-05	28	0.225	2637	0.82	1.05
0.5	0.000102	20	0.183	1788	0.89	1.07
0.8	0.000225	28	0.181	804	0.92	1.10
1	0.000233	23	0.131	562	0.95	1.08
Average						
1mg/l Pb						
0.3	6.15E-05	20	0.206	3348	0.84	1.04
0.5	0.000135	27	0.313	2326	0.78	1.09
0.8	0.000156	19	0.187	1202	0.93	1.11
1	0.00023	23	0.198	864	0.90	1.10
1mg/l Zn						
0.3	0.000144	48	0.152	1054	0.63	0.78
0.5	0.000122	24	0.165	1349	0.84	1.01
0.8	0.000155	19	0.137	881	0.88	1.02
1	0.000137	18	0.148	1079	1.79	1.94

C= (B/A)*100, G= D+F

4.1.5 Conclusion

The results show that the orders of K_ds for suspended materials components namely; bentonite > kaolinite > iron oxide (goethite) (B> K>I) was similar to that previously reported by Garcia, (1978), who found the order of sorption capacity was montmorillonitic > organic > kaolinite = goethite. In addition, Farrah et al., (1980) and Shukla et al., (2000) found that, the sorption capacity of clays was bentonite > illite > kaolinite.

It is not accurate to use K_d value as an indicator of metal uptake when most of the weight of materials used were lost, according to this reason the K_d values of humic acid was not used to compare with other materials.

The results in the preceding sections show that the expanding clay bentonite is by for the most effective material for the removal of Cu, Pb and Zn ions from solution. Almost 100% of the Cu and Pb ions were lost from solution, so the remaining concentration was below the limit of detection by AAS. Therefore only a lower limit for the K_d values for these metals could be estimated by assuming a solution concentration equality the limit of detection for each metal. The K_d values obtained for uptake of these metals on to goethite were surprisingly low. Iron oxide such as goethite is usually thought to have highly adsorptive surfaces. Much of the humic acid used passed through the filter paper, possibly as finely divided collected particle. These were not possible to calculate K_d values for the uptake of these metals on to humic acid.

In the case of kaolinite and goethite it is possible to estimate the variability in the Kd values. This is high, possible due to most of the metal being in solution, and so a small error in analysis with produces a large error in $K_{d.}$ An alternative way of assessing the variability was to use the limit of detection for each element. Using the measured solution concentration (+/-) LOD gave an estimate of variably 70 % for Pb, 25 % for Cu and 5 % for Zn, whichever method is used, there is a high variability associated with the calculated Kd values.

4.2 The model substrates mixed (composite) sample

The experiments were carried out to measure the distribution of copper, lead, and zinc between an aqueous phase and solid phase of mixed material (composite) sediment. This is to understand the influence of different mixed materials on each metal.

4.2.1 Heavy metal sorption behaviour of suspended materials kaolinite and iron oxide (goethite)

The experiment was performed by adding different weights of kaolinite and iron oxide (goethite) (0.2 g -0.8 g, 0.5-0.5 g and 0.8g-0.2 g respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.1.1 Results and discussion

The recovery of materials and distributions of Zn, Cu, and Pb between solid and solution phases are shown in Table 4-5. The K_d values were low. This indicated that smaller quantities of the metals were associated with the suspended particles than the aqueous phase. The results show most of the adsorbent materials were recovered and most of the metal was accounted for. The K_d value of the mixture of kaolinite and iron oxide (goethite) was higher than of the K_d value of the iron oxide (goethite) in the single system. This may be due to iron oxide coating the kaolinite, and an increase the adsorption sites on the kaolinite surface.

Table 4- 5 Recovery of mixed material weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phase for Kaolinite and Iron oxide mixtures

Sample weight (g)	Weight of materials recovered in filter paper (kg)	Recovery of materials (%)	Concentration of metal recovered (mg/l)	weight of metal recovered (mg)	Concentration of metal in materials (mg/kg)	Recovery of metals (mg/l)	Kd (l/kg)
1mg/l Cu							
1K - 0IO	0.00098	98	0.80	0.18	183	0.98	204
0.8K-0.2IO	0.00098	98	0.93	0.02	20	0.95	22
0.5K-0.5IO	0.00097	97	0.92	0.02	20	0.94	22
0.2K-0.8IO	0.000974	97	0.92	0.05	47	0.96	51
0K- 1IO	0.00097	97	1.01	0.03	29	1.04	45
1mg/l Pb							
1K - 0IO	0.00099	99	0.65	0.22	218	0.86	462
0.8K-0.2IO	0.00098	98	0.77	0.06	64	0.83	83
0.5K-0.5IO	0.00097	97	0.76	0.13	128	0.89	168
0.2K-0.8IO	0.00098	98	0.58	0.20	204	0.78	349
0K- 1IO	0.00098	98	0.90	0.03	25.6	0.93	38
1mg/l Zn							
1K - 0IO	0.00096	96	0.87	0.087	79	0.95	142
0.8K-0.2IO	0.00097	97	0.90	0.058	59	0.96	66
0.5K-0.5IO	0.00099	99	0.93	0.034	34	0.97	37
0.2K-0.8IO	0.00097	97	0.98	0.020	20	1.01	21
0K- 1IO	0.00097	97	1.04	0.009	9.2	1.05	18

K=Kaolinite, IO=Iron Oxide

Table 4-6 The weight of metals adsorbed bysingle sorption system and mixed sorption system by kaolinite and iron oxide

Materials	Cu (mg)	Pb (mg)	Zn (mg)
Kaolinite	0.061	0.19	0.070
Iron oxide (goethite)	0.022	0.019	0.005
Mixed (kaolinite and iron oxide)	0.020	0.12	0.03

It is possible to make direct comparison between the weights of each metal taken up by the 0.5 g -0.5 g mixtures and those for 0.5 g of each adsorbant individually. Table 4-6 shows the difference between the single sorption systems and the mixed sorption system. In the kaolinite single sorbent system, sorption of metal by 0.5 g kaolinite was more than the same weight in the single sorption of iron oxide (goethite). On the other hand, sorption of metals by 0.5 g iron oxide (goethite) was less than sorption by the mixed materials. In the mixed materials, the amount of the metal sorbed was less than the sum of the parts. That may be because of changes to the negative charges on the surface of kaolinite occurring when iron oxides accumulate on the surface. Xu and Axe, (2005) and Gallez et al. (1976) suggest that iron oxide coatings reduce the negative charges and increase the positive charges on clay particles. At near neutral pH or high ionic strength iron oxides tend to coagulate (Kumulainen et al., 2008).

Flocculation is the aggregation of fine particles in the aqueous solution system. Flocculation can be attained by different mechanisms, such as approach to the point of zero charge (PZC) and polymer bridging (Rattanakawin et al., 2005). Iron oxide helps to collect the clays particles in flocs (Maa and Pierre, 1992). Iron oxide coating kaolinite can cause aggregation (Sowder et al., 2003). Flocculation is brought about by a decrease in repulsion. The situation of kaolinite is complicated because the different charges between the edges and faces of the particles, depending on the circumstances (Swarten et al., 1974, Van Olphen, 1977; Worrall, 1986).

In the current study three types of aggregation behaviour were observed by visual examination of the mixed systems. A single sediment layer is separated by accumulation in the solution, which happened with 0.8 g kaolinite and 0.2 g iron oxides (goethite). This

may be because the iron oxides coated the adsorption sites of kaolinite, decreasing the sorption capacity. The availability of free adsorption sites on the (0.8 g) kaolinite was coated by 0.2 g of iron oxides (goethite). On the other hand, little flocculation occurred with the mix of 0.8 g iron oxide and 0.2 g kaolinite, possible because of the limited of adsorption sites on the 0.2 g kaolinite. In addition, little flocculation was observed in the solution, from 0.5 g-0.5 g of the mixed materials. In the single sorption system, the sorption of metals and K_d values were low, but in the mixed system these value were even lower due to the flocculation. The result show that the majority of adsorption sites were coated by iron oxide (goethite) which affects sorption of metal and the K_d values on the system mixture of kaolinite and iron oxide (goethite).

The result shows that the affinity order of K_d for the metals for mixtures of kaolinite and iron oxide are (Pb > Zn > Cu). The order was similar to the result of the 0.5 g and 0.8 g of kaolinite, when done individually. On the other hand, a different order was observed Pb > Cu > Zn for the mixture of 0.8 g of iron oxide and 0.2 kaolinite, the order was similar to previous studies Covelo et al, (2007). Covelo et al, (2007) used different conditions such as a range of pH values and large weights to determine adsorption of metal on clay minerals.

Prediction model

A prediction model can used to calculate metal the distributions of in the mixture of kaolinite and iron oxide (goethite). The equation below used to calculate the prediction model in the mixed materials. The prediction model was comparing with actual weight of metal was used in the mixed materials kaolinite and iron oxide (goethite).

$$Kd = \frac{[solid]}{[solution]} 1kg^{-1}$$

$$Kd = \frac{(weight\,of\ \ metal\ in\ solid\ \ material) \div (weight\ of\ \ solid\ \ material)}{(weight\ of\ \ metal\ in\ solution) \div (volume\ of\ \ solution)}$$

$$Kd = \frac{(weight\,of\ \ metal\ in\ solid\ \ material) \times (volume\ of\ \ solution)}{(weight\ of\ \ metal\ in\ solution) \times (weight\ of\ \ solidmaterial)}$$

$$Kd\ = \frac{w \times 1}{(1-w) \times mass\ of\ \ solid\ \ material}$$

$$Kd \times mass\ of\ \ solid\ \ material = \frac{w}{(1-w)}$$

$$w = \frac{Kd \times mass\ of\ \ solid\ \ material}{1 + (Kd \times mass\ of\ \ solid\ \ material)}$$

Table 4-7 The difference between Prediction model and Actual measured in mixed sorption system by kaolinite and iron oxide

Sample weight (g)	Prediction model (mg)	Actual measured (mg)
1mg/l Cu		
1K - 0IO	0.169	0.18
0.8K-0.2IO	0.149	0.02
0.5K-0.5IO	0.115	0.02
0.2K-0.8IO	0.092	0.046
0K- 1IO	0.043	0.028
1mg/l Pb		
1K - 0IO	0.32	0.22
0.8K-0.2IO	0.28	0.06
0.5K-0.5IO	0.21	0.13
0.2K-0.8IO	0.15	0.2
0K- 1IO	0.04	0.03
1mg/l Zn		
1K - 0IO	0.124	0.087
0.8K-0.2IO	0.106	0.0579
0.5K-0.5IO	0.075	0.0342
0.2K-0.8IO	0.055	0.02
0K- 1IO	0.018	0.009

Where w is the weight of metal in solid materials, and $(1-w)$ is the weight of metal in solution. Figure (4-1) to (4-3) shows the actual weight of metals measured in the mixed materials and the weight of metals was calculate by prediction model. The result shows the weights of metals were different in the actual weight and in the prediction model for Cu and Pb (see table 4-7). While the same weight of the metals were observed in the prediction model and in actual system for Zn. That may be because the different between the concentrations of metal measured in the solution and the limit of detection. The different between the concentrations of metal measured in the solution and the limit of detection were high for Cu and Pb, which result different in the actual weight and in the prediction model. On the other hand, the same weight of the metals was observed in the prediction model and in actual system for Zn, because no different between the concentrations of metal measured in the solution and the limit of detection. The prediction model shows the K_d values is not always same in individual component system and in mixed materials system.

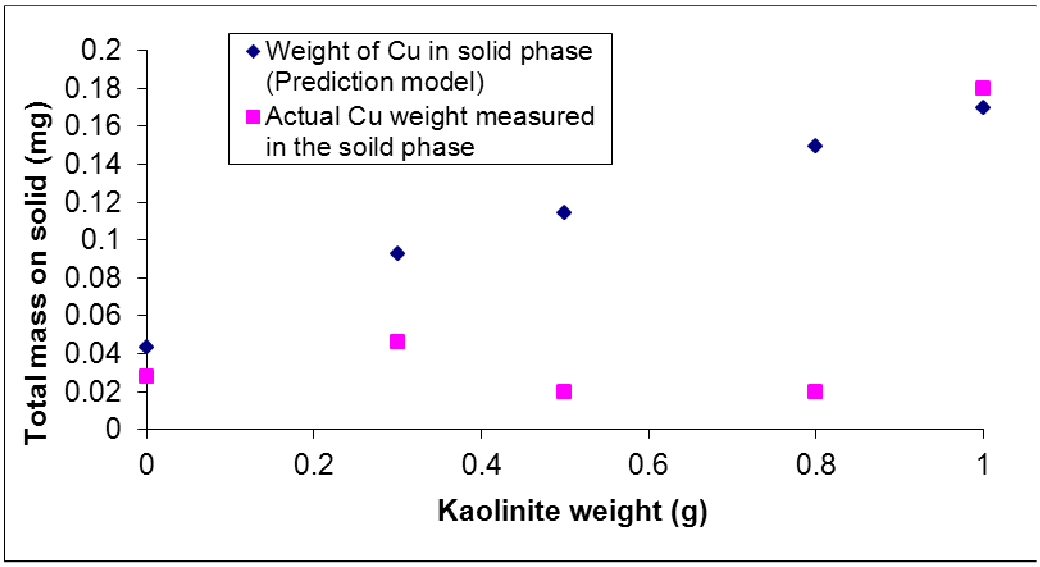

Figure 4-1 weight of Cu (mg) measured on soild phase and in the prediction model.

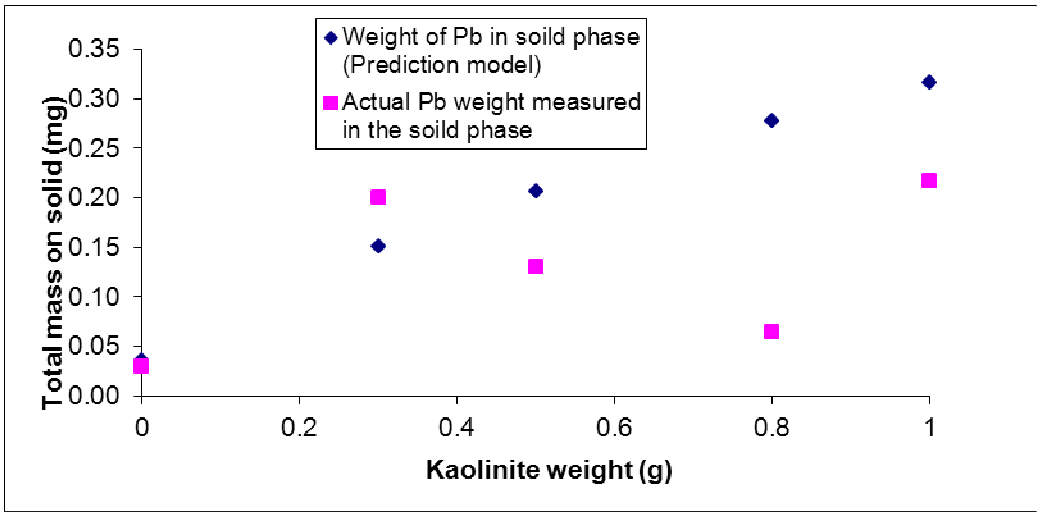

Figure 4-2 weight of Pb (mg) measured on soild phase and in the prediction model.

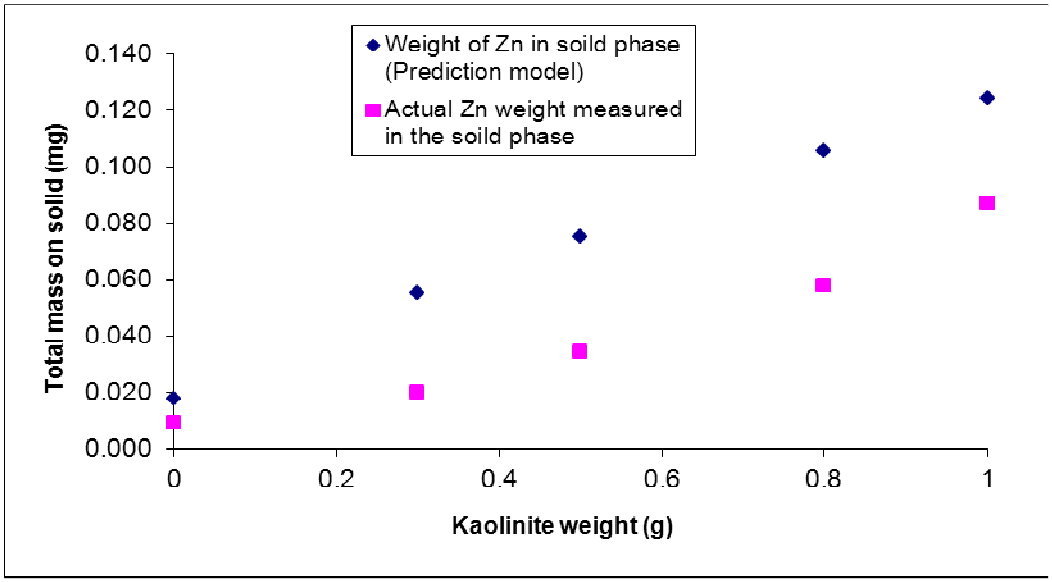

Figure 4-3 weight of Zn (mg) measured on soild phase and in the prediction model.

4.2.2 Heavy metal sorption behaviour of suspended materials kaolinite and bentonite

The experiment was performed by adding different weights of kaolinite to bentonite such as (0.2 g -0.8 g, 0.5-0.5 g and 0.8 g-0.2 g, respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.2.1 Results and discussion

Table 4-8 shows distribution of Zn, Cu, and Pb between metal adsorbed in solid phase and metal concentration in the solution phase and the recovery of materials. Most of the adsorbent material was recovered. Because of the very high adsorption capacity of the bentonite, it is not possible to calculate K_d values for Cu and Pb due to low solution concentrations below the limit of detection.

Table 4- 8 Recovery of mixed materials weights and distribution of Zn, Cu, and Pb between solid materials and solution phase for Kaolinite and bentonite mixtures

A	B	*C	D	E	F	**G
Sample weight	Weight of materials recovered in filter paper	Mixed materials recovery	weight of metal in recovered material	Concentration of metal in kg of mixed material	Concentration of metal in 1 L of filtered water	Kd
(g)	(kg)	(%)	(mg)	(mg/kg)	(mg/l)	(l/kg)
1 mg/l Cu						
0.8K-0.2B	0.000815	81	0.61	748.5	< 0.21	> 3564
0.5K-0.5B	0.000917	91	0.68	740.9	< 0.21	> 3528
0.2K-0.8B	0.00097	97	0.78	804.1	< 0.21	> 3829
1 mg/l Pb						
0.8K-0.2B	0.000815	81	0.64	785.3	< 0.5	> 1570
0.5K-0.5B	0.000917	91	0.73	795.4	< 0.5	> 1590
0.2K-0.8B	0.00096	96	0.83	864.6	< 0.5	> 1729
1 mg/l Zn						
0.8K-0.2B	0.000949	94	0.77	811.2	0.23	3437
0.5K-0.5B	0.000921	92	0.71	770.5	0.21	3534
0.2K-0.8B	0.000963	96	0.83	861.7	0.12	6732

*C= (B/A)*100, K=Kaolinie, B=Bentonite

Table 4-9 The weight of metals adsorbed by 0.5 g single sorption system and 0.5 g mixed sorption system by kaolinite and bentonite

Materials	Cu (mg)	Pb (mg)	Zn (mg)
Kaolinite	0.061	0.19	0.070
Bentonite	0.99	0.75	0.65
Mixed (kaolinite and bentonite)	0.68	0.73	0.71

Table 4-9 shows the difference between the single sorption system and the sorption by the mixed system. In the single component systems, the amount of metal adsorbed by 0.5 g of kaolinite was less than the amount adsorbed by 0.5 g of bentonite. In addition, the amount of metal adsorbed by the mixed materials was less than the amount of metal adsorbed by the sum of the parts. That may be because kaolinite is blocking the metal ions from reaching the binding sites on the bentonite. In this experiment the adsorption capacity of the bentonite for Cu and Pb were high and most of metals concentration was measured in the solid phase and low metals concentration were measured in solution phase, which resulted the concentration lower than the detection limit.

4.2.3 Heavy metal sorption behaviour of suspended materials kaolinite and humic acid

The experiment was performed by adding different weights of kaolinite and humic acid (0.2 g-0.8 g, 0.5-0.5 g and 0.8 g-0.2 g respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.3.1 Results and discussion

The distribution of Zn, Cu, and Pb between the solid and solution phases and the recovery of materials are shown Table 4-10. Substantial amounts of the adsorbent materials were not recovered. It is likely that most of the humic acid was not recovered; while the recovered materials could be mainly kaolinite, in this case it is not possible to calculate K_d values. Most of the metals were accounted for. The majority of the metal concentration was measured in the solution phase and low concentrations measured in solid phase; this indicated a smaller amount of the metals were linked with the suspended materials.

Table 4- 5 Recovery of mixed material weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phase Kaolinite and Humic acid mixtures

	A	B	C	D	E	F
	Sample weight	Weight of materials recovered in filter paper	Mixed materials recovery	weight of metal in recovered material	Concentration of metal in kg of mixed material	Concentration of metal in 1 L of filtered water
	(g)	(kg)	(%)	(mg)	(mg/kg)	(mg/l)
1 mg/l Cu						
0.2K-0.8HA		0.000308	30	0.072	233	0.97
0.5K-0.5K		0.000382	38	0.132	345	0.92
0.8K-0.2HA		0.000837	83	0.146	174	0.89
1 mg/l Pb						
0.2K -0.8HA		0.000364	36	0.248	682	0.82
0.5K-0.5HA		0.000560	56	0.237	423	0.84
0.8K-.2HA		0.000829	83	0.223	270	0.79
1 mg/l Zn						
0.2K-0.8HA		0.000397	39	0.152	382	0.86
0.5K-0.5HA		0.000553	55	0.106	191	0.89
0.8K-.2HA		0.000857	85	0.071	83.7	0.87

C= (B/A)*100, K=Kaolinite, HA=Humic Acid

Table 4-11 The weight of metals adsorbed by 0.5 g single sorption system and 0.5 g mixed sorption system by the kaolinite and humic acid

Materials	Cu (mg)	Pb (mg)	Zn (mg)
Kaolinite	0.061	0.19	0.070
Humic acid	0.183	0.313	0.165
Mixed (kaolinite and humic acid)	0.132	0.237	0.106

Table 4-11 shows the differences between the single sorption systems and the mixed sorption system. In the single systems, the amount of metal adsorbed by 0.5 g of humic acid was higher than the amount of metal adfsorbed by same weight of kaolinite. In the mixed materials, the amount of metal sorption was higher than the same weight of kaolinite in the single system. In contrast the sorption of metal was less than the same weight of humic acid single system; moreover, the sorption of metal in the mixed materials was less than the sum for the parts. This result may be due to the presence of small a amount of humic acid with the mixed materials since most of humic acid weight was lost through the filter paper.

4.2.4 Heavy metal sorption behaviour of suspended materials bentonite and iron oxide (goethite)

The experiment was performed by adding different weights of bentonite and iron oxide (goethite) (0.2 g-0.8 g, 0.5-0.5 g and 0.8 g-0.2 g, respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.4.1 Results and discussion

Table 4-12 shows the distribution of Zn, Cu, and Pb between the solid and solution phases and the recovery of materials. Most of the metals were accounted for and most of the adsorbent material was recovered. The results indicated that the K_d value for Zn of the bentonite and iron oxide (goethite) in the single system was lower than the K_d value of the

bentonite and iron oxide mixture. This increase in K_d value of the mixture is possibly because iron oxide (goethite) coated the bentonite, which introduced some adsorption sites on the surface of the bentonite, and increased the specific surface area (Zhuang and Yu, 2002; Olu-Owolabi et al., 2010). Iron oxide coatings on clay particles can increase the positive charges and decreased the negative charges at pH below point of zero charge (PZN). The aggregation of clay particles in the presence of iron oxide could increase the specific surface area, leading to an increase of the adsorption capacity of cations.

In the current study high flocculated with the mixture of (0.8 g) iron oxide and (0.2 g) bentonite. This may be because of the (0.8 g) iron oxide (goethite) coating all of the surface sites on the (0.2 g) bentonite. Alternatively, a smaller amount of the particles flocculated with (0.2 g) iron oxide (goethite) and (0.8 g) bentonite. This may be because of the high availability of adsorption sites with a mixture of (0.8 g) bentonite and the smaller number of iron oxides coated with small weight (0.2 g). In other words, there was a lot of the particle surface area not coated by the iron oxide ions. This may be because the total amounts of adsorption sites were more than the amount of iron oxide (goethite) and there were enough surface adsorption sites available with a large amount of bentonite.

Table 4- 6 Recovery of mixed materials weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phasen for bentonite and iron oxide mixtures

A	B	C	D	E	F	G
Sample weight	Weight of materials recovered in filter paper	Mixed materials recovery	weight of metal in recovered material	Concentration of metal in kg of mixed material	Concentration of metal in 1 L of filtered water	Kd
(g)	(kg)	(%)	(mg)	(mg/kg)	(mg/l)	l/kg
1 mg/l Cu						
0.2B -0.8IO	0.00099	99	0.63	632	< 0.21	> 3009.6
0.5B-0.5IO	0.00098	98	0.74	749	< 0.21	> 3567.0
0.8B-0.2IO	0.00097	97	0.75	767	< 0.21	> 3654.0
1 mg/l Pb						
0.2B -0.8IO	0.0099	99	0.62	627	< 0.5	> 1255.6
0.5B-0.5IO	0.00097	97	0.84	867	< 0.5	> 1734.0
0.8B-0.2IO	0.00095	95	0.85	565	< 0.5	> 1130.1
1 mg/l Zn						
0.2B-0.8IO	0.00099	99	0.83	833	0.26	3207.1
0.5B-0.5IO	0.00097	97	0.89	913	0.173	5279.7
0.8B-0.2IO	0.00072	72	0.79	1085	0.036	30143.5

C= (B/A)*100, B=Bentonite, IO=Iron Oxide

Table 4-7 The weight of metals adsorbed by 0.5 g single sorption system and 0.5 g mixed sorption system by the bentonite and iron oxide

Materials	Cu (mg)	Pb (mg)	Zn (mg)
Bentonite	0.99	0.75	0.65
Iron oxide (goethite)	0.022	0.19	0.005
Mixed (bentonite and iron oxide)	0.74	0.84	0.89

Table 4-13 shows the differences between the single sorption systems and the mixed sorption system. In the single system, sorption of metal by 0.5 g bentonite was more than the same weight in the single sorption of iron oxide (goethite). In the mixed system the metal adsorbed was less than the sum of the parts. Eren et al., (2009) suggested that some factors, such as the presence of the surface coating and differences in surface area between the materials can affect the adsorption of heavy metals in the mixed materials. Bradley and Lewin, 1982 suggested that a change in the total surface covering by metals could affect the correlation between the heavy metal concentration and suspended particle concentration.

4.2.5 Heavy metal sorption behaviour of suspended materials bentonite and humic acid

The experiment was performed by adding different weights of bentonite and humic acid (0.2 g-0.8 g, 0.5-0.5 g and 0.8 g-0.2g, respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.5.1 Results and discussion

The recovery of materials and distributions of Zn, Cu, and Pb between solid and solution phases are shown Table 4-14. The majority of the metals were found in the solution, which means little of metal ions associated with the suspended phase. Large amounts of the adsorbent materials were not recovered; mainly the humic acid materials were lost, while the recovered materials might be predominately bentonite. The sorptions values were different with different quantities of mixed materials and different metals.

Table 4- 8 Recovery of mixed materials weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phase for bentonite and humic acid mixtures

A	B	C	D	E	F
Sample weight	Weight of materials recovered in filter paper	Mixed materials recovery	weight of metal in recovered material	Concentration of metal in kg of mixed material	Concentration of metal in 1 L of filtered water
(g)	(kg)	(%)	(mg)	(mg/kg)	(mg/l)
1 mg/l Cu					
0.2B -.8HA	0.0003799	73	0.086	226	0.92
0.5B- 0.5HA	0.0005551	55	0.108	194	0.86
0.8B-0.2HA	0.0006715	67	0.164	244	0.87
1 mg/l Pb					
0.2B -.8HA	0.0003799	37	0.185	487	0.86
0.5- 0.5g	0.0005777	57	0.229	396	0.84
0.8B-0.2HA	0.0006432	64	0.208	323	0.77
1 mg/l Zn					
0.2B-.8HA	0.0003767	37	1.05	2787	0.81
0.5B-0.5HA	0.0006045	60	0.934	1545	0.78
0.8B-.2HA	0.0008475	84	0.636	750	0.33

*C= (B/A)*100, B=Bentonite, HA=Humi Acid

Table 4-9 The weight of metals adsorbed by 0.5 g single sorption system and 0.5 g mixed sorption system by the bentonite and humic acid

Materials	Cu (mg)	Pb (mg)	Zn (mg)
Bentonite	0.99	0.75	0.65
Humic acid	0.183	0.313	0.165
Mixed (bentonite and humic acid)	0.108	0.229	0.934

Table 4-15 shows the single sorption and the mixed sorption material of the bentonite and humic acid. The results indicated that the metal sorption was lower in the mixed materials compared with single sorption system, except for Zn, for which the sorption was higher in the mixed system than the single sorption system. The decrease of metal adsorption may be because of the presence of humic acids, which could have decreased the specific surface area of the bentonite by blocking access to the adsorbing sites (Abate and Masini 2005, Zhuang and Yu, 2002, Liu and González, 1999).

4.2.6 Heavy metal sorption behaviour of suspended materials iron oxide and humic acid

The experiment was performed by adding different weights of iron oxide (goethite) and humic acid (0.2 g-0.8 g, 0.5-0.5 g and 0.8 g-0.2g, respectively) to one litre of deionised water containing 1 mg/l concentration of metal. The procedure is described in section 2.5.2.

4.2.6.1 Results and discussion

Table 4-16 shows the recovery of materials and distribution of Zn, Cu, and Pb between solid and solution phases. The majority of the materials in the mixture of iron oxide and humic acid were not recovered. The majority of the concentrations were measured in the solution phase, which means few of the metals were linked with the suspended phase.

Table 4- 10 Recovery of mixed materials weights and distribution of (Zn, Cu, and Pb) metals between solid and solution phase for iron oxide and humic acid mixtures

A	B	C	D	E	F
Sample weight	Weight of materials recovered in filter paper	Mixed materials recovery	weight of metal in recovered material	Concentration of metal in kg of mixed material	Concentration of metal in 1 L of filtered water
(g)	(kg)	(%)	(mg)	(mg/kg)	(mg/l)
1 mg/l Cu					
0.8HA-0.2IO	0.0003588	36	0.408	1137	0.93
0.5HA- 0.5IO	0.0006036	60	0.234	387	0.84
0.2HA-0.8IO	0.0008493	85	0.140	164	0.64
1 mg/l Pb					
0.2IO-0.8HA	0.0003255	32	0.327	1007	0.67
0.5IO -0.5 HA	0.0005912	59	0.312	528	0.76
0.8IO-0.2HA	0.0008340	83	0.434	520	0.50
1 mg/l Zn					
0.2IO-0.8HA	0.0003717	37	0.182	489	0.78
0.5IO-0.5HA	0.0006681	66	0.268	401	0.72
0.8IO-0.2HA	0.0008736	87	0.140	160	0.79

C= (B/A)*100, HA=Humic Acid, IO=Iron Oxide

Table 4-11 The weight of metals adsorbed by 0.5 g single sorption system and 0.5 g mixed sorption system by the iron oxide and humic acid

Materials	Cu (mg)	Pb(mg)	Zn(mg)
Iron oxide (goethite)	0.022	0.19	0.005
Humic acid	0.183	0.313	0.165
Mixed (iron oxide and humic acid)	0.23	0.312	0.268

Table 4-17 shows the single sorption of iron oxide and humic acid and sorption of the mixed material for both iron oxide and humic acid. The sorption of metals in the mixed materials was higher than the sorption in the single sorption system; in contrast sorption of metals was less than the sum of the parts. The results indicated that the adsorption increased in the mixed materials compared with single sorption system of iron oxide or humic acid. Increased or decreased adsorption of metal by humic acid or iron oxide mixture is controlled by the experimental conditions (Saito et al., 2005). Orsetti et al, (2006), and Alcacio et al. (2001) suggested that the interaction between humic acid and iron oxide causes the formation of complexes (Varadachari et al., 2000; Saito et al., 2004; Fu and Quan, 2005).

4.2.7 Discussion

It is possible to calculate K_d values only for the mixed kaolinite – iron oxide system, because bentonite removes metals from solution to a concentration below the detection limit, and the humic acid is too soluble. In all cases, mixtures of kaolinite and iron oxide result in a K_d value lower than kaolinite alone (Table 4-5).

It is also possible to use the K_d values calculated individually for kaolinite and iron oxide in order to calculate the mass of metal held on the solid phase in mixtures of the two, and to compare this value with the mass of metal measured. In all cases the measured mass is low than the prediction mass, suggesting that the sorptive proportion of the materials are different in mixtures compared to the materials alone.

Direct comparison of the mass of metal held on the solid phase can be made for 0.5 g material alone and the 0.5 g- 0.5 g mixtures. Table 4-6, 4-9, 4-11, 4-13, 4-15 and 4-17 suggest that interaction between materials can both increase and decrease the mean of metal held. This may be due to masking of binding sites (decrease) or expansive of binding sites due to flocculation (increase).

4.2.8 Conclusion

This study tries to simulate the natural system, exploring the effects of trace metals on important materials, which are commonly found in the soil. The studies evaluate heavy metal adsorption in single sorption systems, and in mixed systems of clays, humic material and iron oxide. The results indicate that the adsorption capacity of bentonite clay is more than all of other components with an observed adsorption capacity sequence of bentonite > kaolinite > iron oxide (goethite). This was consistent with previously reported results by Garcia et al., (1978), who repoted on order of sorption as montmorillonitic > organic > kaolinite – goethite. In addition, Farrah et al., (1980) and Shukla, (2000) found that the sorption order was montmorillonite> illite > kaolin.

In the bentonite mixed system is not possible to calculate accurate K_d value where, bentonite sorbs most of the metals in the solution. While in the mixed system of humic acid the high mobility of humic acid is effect the K_d value for the mixed materials. On the other hand, metal adsorbed in the mixed materials was little increased with increasing the humic acid. That may be because of humic acid coated increasing the active surface for metal sorption on the kaolinite surface. Hizal and Apak, (2006) suggested sorbs of metal increase in presence humic acid with kaolinite of because the mixed behaved more like a chelating ion exchanger comparing with kaolinite single sorption system.

In the mixed system the results indicate that the K_d values were different for each metal. In general the K_d values were different, under the same conditions of fixed concentrations and different mixed material weights. This is an important observation, which suggests that in studies of natural systems the use of Kd values for individual sorbent materials may not be valid. It may be more appropriate to assess metal uptake based on likely mixtures of materials that actually exist in the natural systems.

Chapter 5

The role of the fine suspended sediment in the transport of metals

5 River Water Samples

This chapter explores the role of suspended sediment in the transport of metals in the River Kelvin tributaries. The investigation focuses on metals in different size fractions of the particulate phase in surface waters. Sediments play the main role as a sink and possible source of trace metals in many rivers. Study of factors such as the carrying capacity and nature of suspended particles is essential in attempting to understand the impact of the metals they carry on water systems (Pertsemli & Voutsa, 2007). Suspended sediments were collected by filtration and analyzed for Ca, Fe, K, Mg, Mn and Zn contents, based on data obtained during a 2009 and 2010 sampling period. In this chapter Cu and Pb were not determined, because low concentrations were measured in the first two months of the sampling period. The results are divided into three sections, beginning with the weight of suspended sediment per unit volume of water in different tributaries and different sampling months. The second section will look at the concentration of metals in the mass of suspended sediment defined in two size ranges. The last section will focus on the concentration of metals in a volume of water associated with that sediment in the river water samples. Sediment mass was used together with metal concentration data to define the metal loads in the different size fractions.

Table 5-1 and Table 5-2 show the average rainfall (mm) in the Glasgow area (Met office) and Daily flow rate from some tributaries (SEPA, 2011). The data show the monthly average of the rainfall and the weather description of the sampling day (see Appendix 1 and Appendix 2 daily rainfall amount in Glasgow University area and Daily flow rate amount from some tributaries). The table indicates that the average rainfall in July, August and November 2009 was high.

Table 5- 1 Average rainfall (mm) in the Glasgow area determined at Glasgow Airport and University of Glasgow

Months	Rainfall mm		Date of sampling
	Glasgow* Airport	Glasgow University	
1/2009	137	70	13/6/2009
2/2009	23	22	
3/2009	98	67	14/7/2009
4/2009	55	47	
5/2009	107	71	
6/2009	38	21	
7/2009	120	85	15/8/2009
8/2009	173	140	
9/2009	69	54	14/9/2009
10/2009	100	80	
11/2009	251	195	
12/2009	65	41	16/11/2009
1/2010	52	44	
2/2010	77	65	
3/2010	75	63	10/2/2010
4/2010	81	48	
5/2010	17	19	24/3/2010
6/2010	30	26	
7/2010	132	65	
			5/5/2010
			8/6/2010

(* Met office, http://www.metoffice.gov.uk/climate/uk/)

Table 5- 2 Daily flow rate value (m^3/s) before and after sampling time (SEPA, 2011).

Date	Allander	Glazert	Bothlin	Luggie
11/06/2009	0.093	0.193	0.085	0.148
12/06/2009	0.081	0.189	0.081	0.145
13/06/2009	**0.111**	**0.188**	**0.081**	**0.146**
14/06/2009	0.090	0.263	0.088	0.238
12/07/2009	0.235	0.922	0.169	0.212
13/07/2009	0.329	2.175	0.350	0.648
14/07/2009	**0.390**	**1.326**	**0.325**	**0.322**
15/07/2009	0.329	0.636	0.278	0.307
13/08/2009	0.242	0.404	0.340	0.524
14/08/2009	7.351	14.262	2.644	4.565
15/08/2009	**4.017**	**6.793**	**2.674**	**3.867**
16/08/2009	1.666	2.440	1.195	1.257
17/08/2009	1.430	2.620	0.996	1.052
11/09/2009	0.979	1.228	0.691	0.735
12/09/2009	0.745	0.896	0.558	0.597
13/09/2009	0.579	0.742	0.475	0.508
14/09/2009	**0.487**	**0.664**	**0.428**	**0.440**
15/09/2009	0.416	0.589	0.375	0.385
15/11/2009	1.173	1.800	0.930	1.098
16/11/2009	**2.194**	**4.322**	**1.155**	**1.681**
17/11/2009	3.600	6.421	1.592	2.311
07/02/2010	0.664	1.380	0.611	0.906
08/02/2010	0.540	0.864	0.534	0.759
09/02/2010	0.445	0.645	0.489	0.598
10/02/2010	**0.371**	**0.562**	**0.393**	**0.469**
11/02/2010	0.348	0.498	0.337	0.394
23/03/2010	0.488	1.112	0.227	0.320
24/03/2010	**0.833**	**2.232**	**0.229**	**0.350**
25/03/2010	0.817	1.909	0.303	0.512
04/05/2010	0.189	0.295	0.229	0.233
05/05/2010	**0.187**	**0.290**	**0.234**	**0.238**
06/05/2010	0.183	0.282	0.225	0.230
07/06/2010	0.128	0.164	0.156	0.159
08/06/2010	**0.180**	**0.274**	**0.273**	**0.333**
09/06/2010	0.162	0.395	0.185	0.226

5.1 The suspended sediment weight

The objective in this part was to investigate the variation between suspended sediment masses in different seasons. Sediment masses were collected in two ranges >1.2 µm diameter and between 1.2 µm and 0.2 µm in diameter of the filter paper, at different sampling sites and in different sampling months. The sediment masses were obtained to define the influence of particle size in explaining the mechanism of metal fluvial distribution. Other researchers have used many types of filter paper to collect suspended sediment samples for metal determination. Different research uses different filter paper size. For example, samples have been collected by:

1. Whatman GFR filters 1.6 µm (Bradley and Lewin, 1982);
2. Whatman 0.45 µm glass fibre filters (Warren, 1981);
3. Millipore filters 0.45 µm pore size (Dassenakis et al., 1996);
4. Whatman polycarbonate membrane filter 0.2 µm (Naganoa et al., 2003);
5. 0.2 µm cellulose acetate filters (Radakovitch et al., 2008);

The current research used filter paper of two different pore sizes to collect particles larger than 1.2 µm in diameter and particles between 1.2 µm and 0.2 µm in diameter. The masses of the suspended sediment in the river water are presented in this section of the chapter.

Figure 5-1 shows the seasonal variation in mass of suspended sediment from Craigton Burn. The mass of suspended sediment in the > 1.2 µm fraction increases in the summer season for both 2009 and 2010, but is relatively constant in the rest of the sampling months. The mass of suspended sediment in the 1.2 µm to 0.2 µm fraction is higher than the mass of suspended sediment in the > 1.2 µm fraction in August 2009, February and March 2010. The mass of suspended sediment in the > 1.2 µm and in the 1.2 µm to 0.2 µm fraction was equal in September 2009 and May 2010.

The sediment mass in the 1.2 µm - 0.2 µm fraction is high in August 2009. The high rainfall increases the mass of sediment particles, large and small alike, and perhaps because the large particles deposit rapidly the fine sediment mass dominates. The mass of sediment was high in February and March with low rainfall. The March sample was collected at the end of the month, with significant snowfalls, that may increase the fine sediment transport more than the large particle transport. That may be because of the presence of snow, which reduces velocity of river flow; as a result there is an increase in large sediment deposition and increase in fine sediment transport. The suspended sediment delivered during snowmelt conditions is more finely grained than during rainfall (Hillel, 2004).

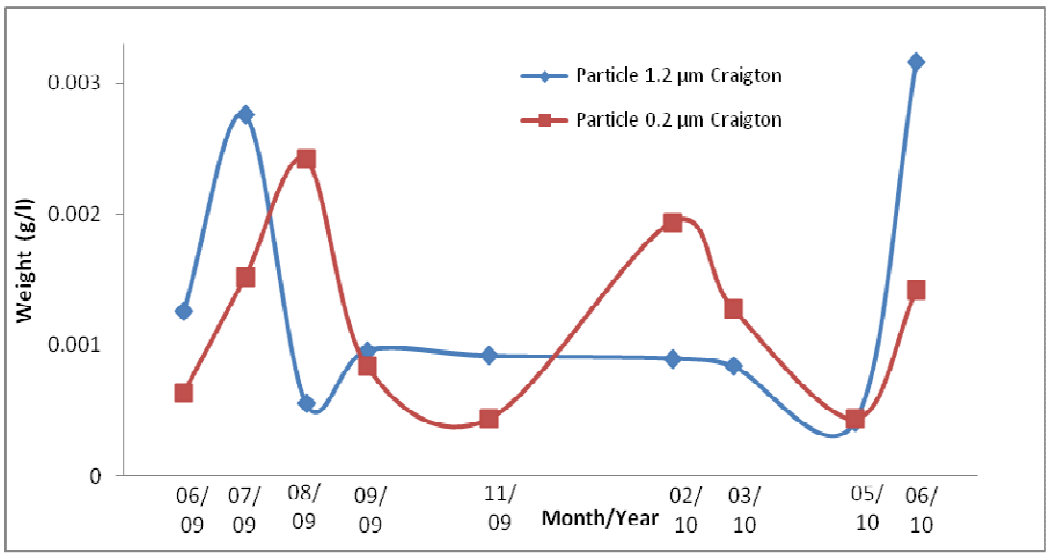

Figure 5- 1 Mass of suspended sediment (g/ l) in the > 1.2 µm and in the 1.2 - 0.2 µm diameter size fractions from Craigton Burn

Figure 5-2 shows the mass of suspended sediment in the two size fractions and Figure 5-3 shows the variation of mass of suspended sediment with flow rate from Allander Water. The mass of the suspended sediment in the two size fractions tends to be higher in the summer season, but the mass is relatively stable in the rest of the sampling months. High flow rate would increase the mass of sediment of both large and small particles, but the large particles would respond more quickly to lower flow. Increase flow rate does not always cause increase in mass and decrease flow rate does not always cause decrease in the mass of sediment. The flow rate was high in August and November but the mass of sediment was low in the > 1.2 fraction.

On the other hand, in the range 1.2 - 0.2 µm the mass of sediment was high with high flow rate in August and the mass of sediment was low in November with high flow rate. Higher mass sediment in the > 1.2 µm in June and July with low flow rate (0.390 m^3/s). The mass of sediment is stable in the rest of the sampling months. The mass slightly increased in June 2010 with flow rate (0.180 m^3/s). The mass of the suspended sediment in the range 1.2 - 0.2 µm is higher than the sediment mass in the > 1.2 µm fraction in August and September 2009. That may be because of high flow rate before the sampling day (7.35 m^3/s), which carries the coarse sandy sediments such as quartz and feldspar. The coarse materials are fast deposited because of the weight and decrease the flow rate to (4.01 m^3/s), which may increase the fine sediment in the solution.

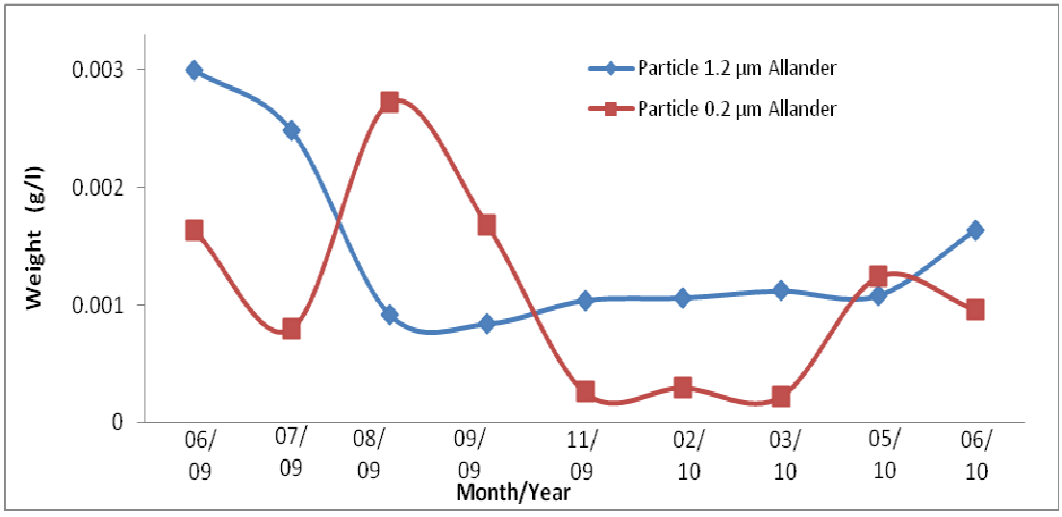

Figure 5- 2 Mass of suspended sediment (g/ l) in the > 1.2 µm and 1.2 µm - 0.2 µm diameter size fractions from Allander water.

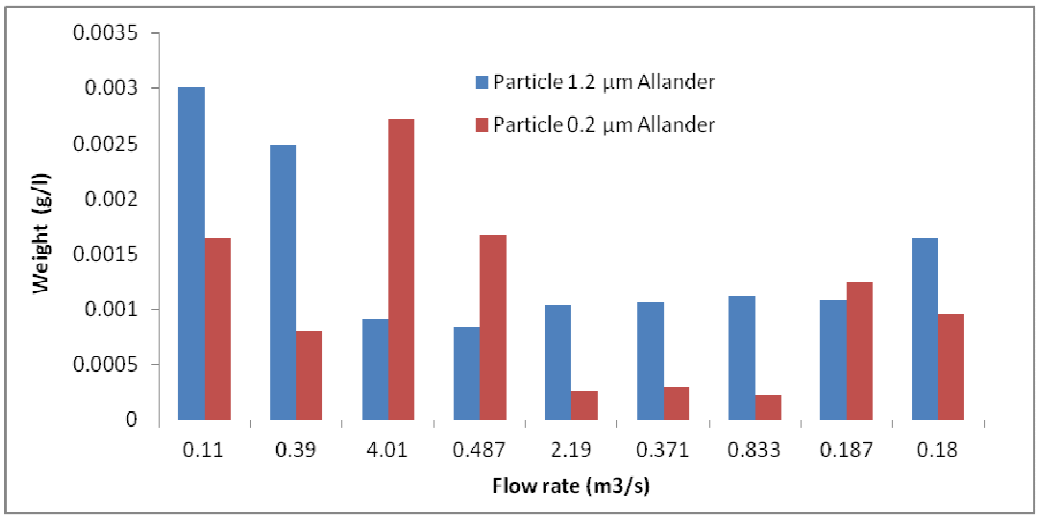

Figure 5- 3 Variation of mass of suspended sediment (g/ l) with flow rate of water for the > 1.2 µm and in the range 1.2 µm to 0.2 µm sediment from Allander Water.

Figure 5-4 compares the sediment from Craigton Burn and Allander water. This is of interest because the sampling sites are near to the intersection of the two rivers. The masses of the sediment in the > 1.2 µm fractions in the two rivers show a similar trend. The mass of the larger fraction is similar in both rivers. The big differences seem to be the higher mass of small particles in Craigton Burn compared to Allander water over the winter of 2009/10. The sediment mass in the > 1.2 µm fractions is higher in June and July 2009, after that the mass was relatively constant in the rest of the sampling months. The mass of the sediment in the 1.2 - 0.2 µm fraction was similar in both rivers with small divergence, where in Craigton Burn the mass of sediment was higher than the mass in Allander Water in February 2010. On the other hand, the mass of sediment was higher in Allander Water than Craigton Burn in May 2010. The mass of the sediment in the 1.2 - 0.2 µm fraction exceeds that in the > 1.2 µm fraction in August for both tributaries.

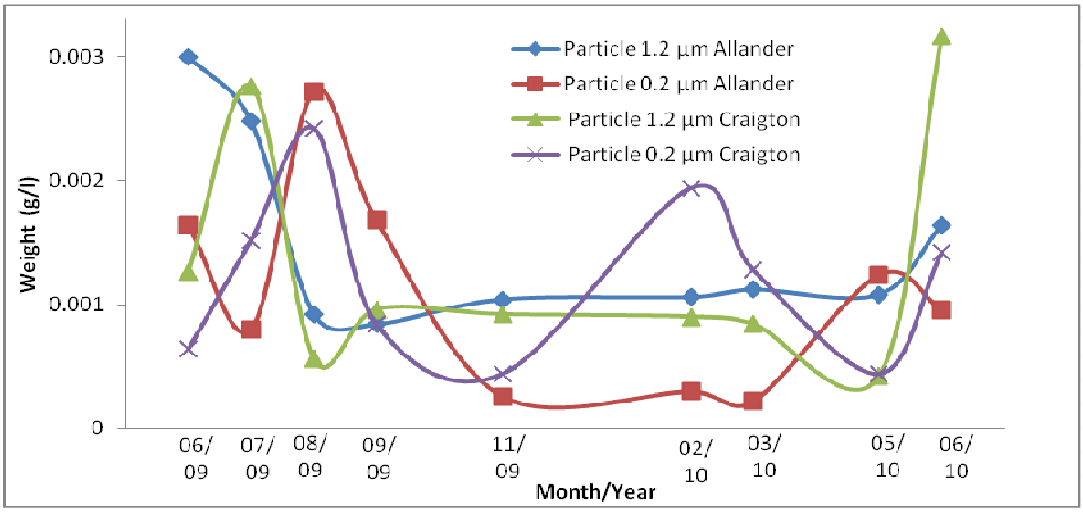

Figure 5- 4 Mass of suspended sediment (g/ l) in the > 1.2 µm and in the 1.2 - 0.2 µm fractions from Craigton Burn and Allander Water.

Figure 5-5 shows the mass of the suspended sediment with diameter > 1.2 µm and in the range 1.2 - 0.2 µm from Craigmaddie Burn. The sediment mass is similar in June 2009 for the two size fractions. The sediment mass in the > 1.2 µm fraction increased in November 2009. This may be because of the effect of the rainfall amount in November. On the other hand, in August 2009 the mass of sediment in the 1.2 µm to 0.2 µm diameter fractions was higher than the mass of sediment in the > 1.2 µm fraction. The sediment mass is relatively constant in the rest of the sampling months.

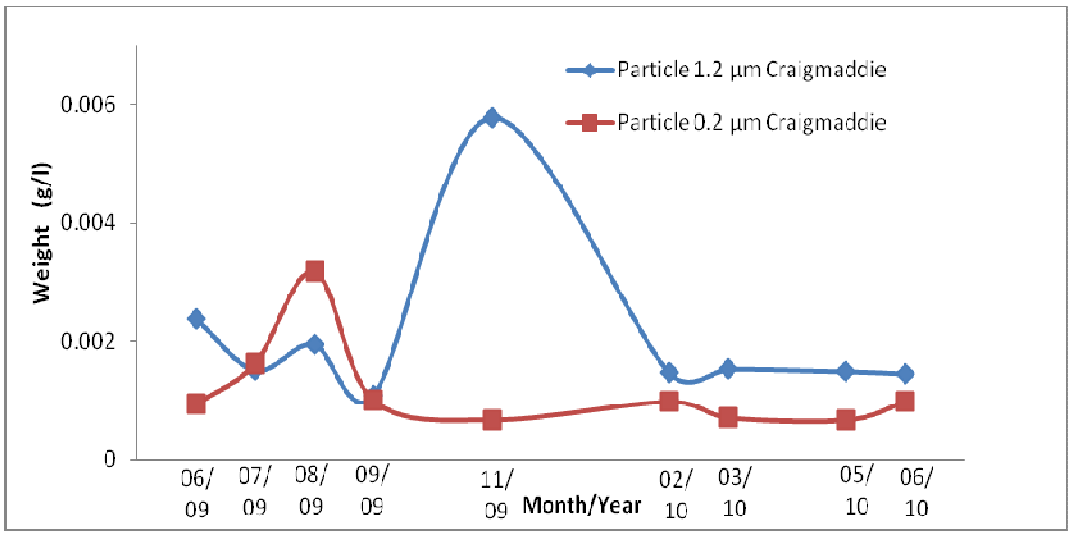

Figure 5- 5 Mass of suspended sediment (g/ l) in the > 1.2 µm and in the range 1.2 µm to 0.2 µm from Craigmaddie Burn.

The masses of sediment in the > 1.2 µm diameter and in the 1.2 µm to 0.2 µm sizes fractions from Glazert water are shown in Figure 5-6 and Figure 5-7 shows the variation of mass of suspended sediment with flow rate. There is no strong relationship between the flow rate and mass of sediment. The flow rate was highest in August (6.79 m^3/s) but the mass of sediment was low in the > 1.2 fraction. On the other hand, in the range 1.2 - 0.2 µm the mass of sediment was low with the high flow rate in November (4.32 m^3/s). In addition, the flow rate was low in June (0.274 m^3/s) 2010 in the 1.2 - 0.2 µm fraction but the mass of sediment was high. The sediment mass was higher in the > 1.2 µm fraction in June and November 2009 compared with other sampling months. In July 2009 high flow rate (1.32 m^3/s) increased the mass of sediment in both size fractions. The high flow rate (4.32 m^3/s) caused a higher mass of particles in November 2009 in the > 1.2 µm fraction. The particle mass in the range 1.2 µm to 0.2 µm was higher than sediment mass in the > 1.2 µm diameter in August 2009. The higher 1.2 µm to 0.2 µm mass in August 2009 may be because of high flow rate before the sampling day, which carries large and fine sediments. But the flow rate was decreased from (14.26 m^3/s) before the sampling day to (6.79 m^3/s) on the sampling day. While in June 2010 the mass of sediment increased in the large and fine sediment with low flow rate (0.274 m^3/s.

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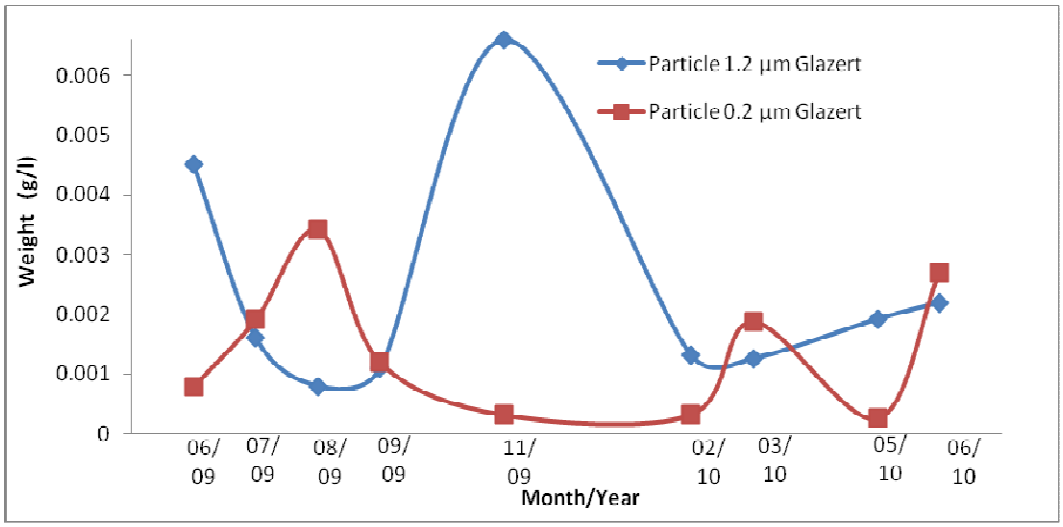

Figure 5- 6 Mass of suspended sediment (g/ l) in the > 1.2 µm and in the range 1.2 – 0.2 µm diameter size fractions from Glazert water.

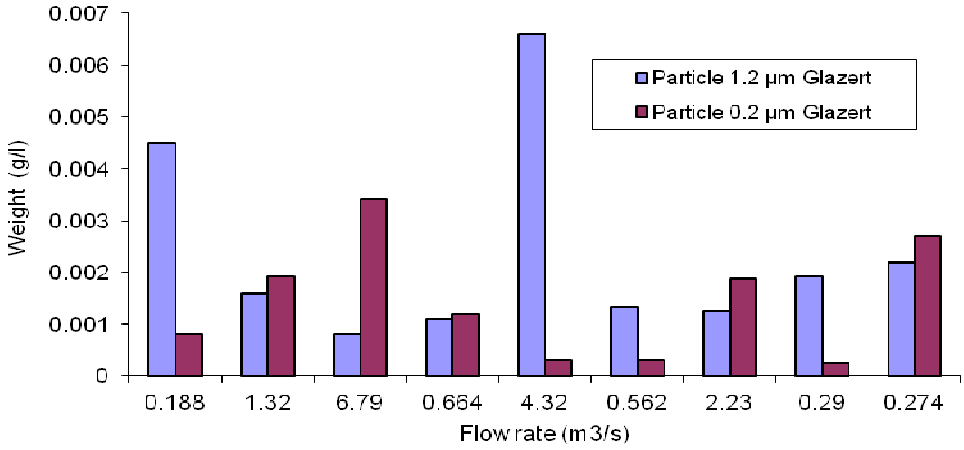

Figure 5- 7 Variation of mass of suspended sediment (g/ l) with flow rate of water for the > 1.2 µm and in the range 1.2 µm to 0.2 µm sediment from Glazert Water.

Figure 5-8 shows the mass of sediment in the > 1.2 µm diameter and in the 1.2 µm to 0.2 µm sizes fraction from Bothlin Burn and Figure 5-9 shows the variation of mass of suspended sediment with flow rate. The flow rate was high in August (2.67 m^3/s) but the mass of sediment was low in the > 1.2 fraction. In addition, the flow rate was high in November (1.15 m^3/s) and the mass of sediment was low in the > 1.2 fraction. The mass of sediment in the >1.2 µm fraction was higher in July 2009 with low flow rate (0.325 m^3/s). In addition, the sediment mass was higher in September and November 2009 after that the mass gradually decreased in the rest of the sampled months. The flow rate in September 2009 had a gradual decrease from two days before the sampling day from (0.558 m^3/s) until the day after the sampling (0.375 m^3/s). While in November 2009 the flow rate was high (1.15 m^3/s) on the sampling day which explains the increase in mass of the >1.2 µm fraction. On the other hand, the mass of the suspended sediment in the range 1.2 µm to 0.2 µm is higher than the mass sediment in the >1.2 µm in June 2009. The mass of the sediment in the >1.2 µm and in the range 1.2 µm to 0.2 µm was similar in August 2009 (2.67 m^3/s). That may be because high flow rate carries large and fine sediments. In addition, in May and June 2010 the mass of sediment is similar in the >1.2 µm and in the range 1.2 µm to 0.2 µm with low flow rate.

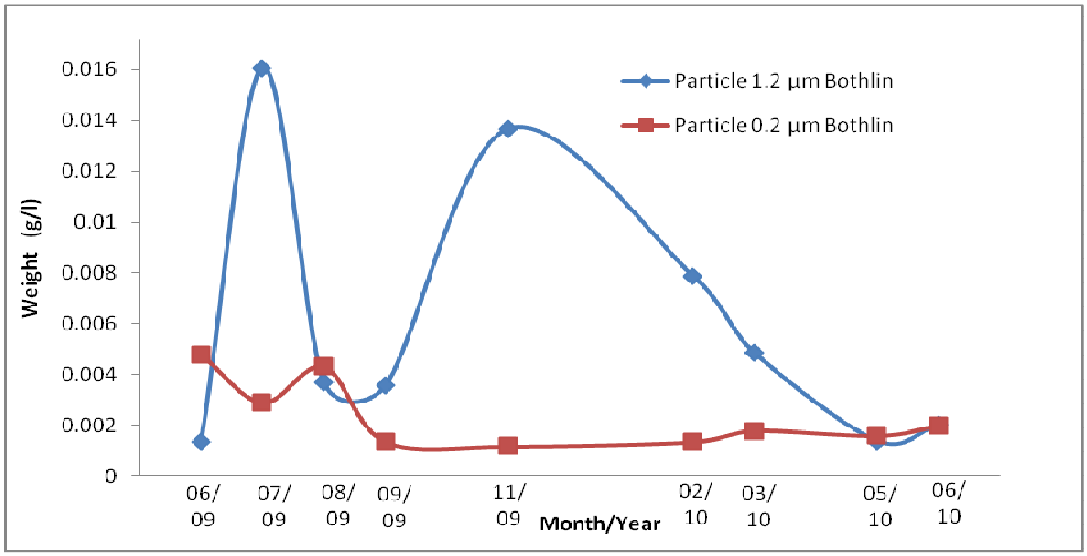

Figure 5- 8 Mass of suspended sediment (g/ l) water in the > 1.2 µm and in the 1.2 – 0.2 µm fractions from Bothlin Burn.

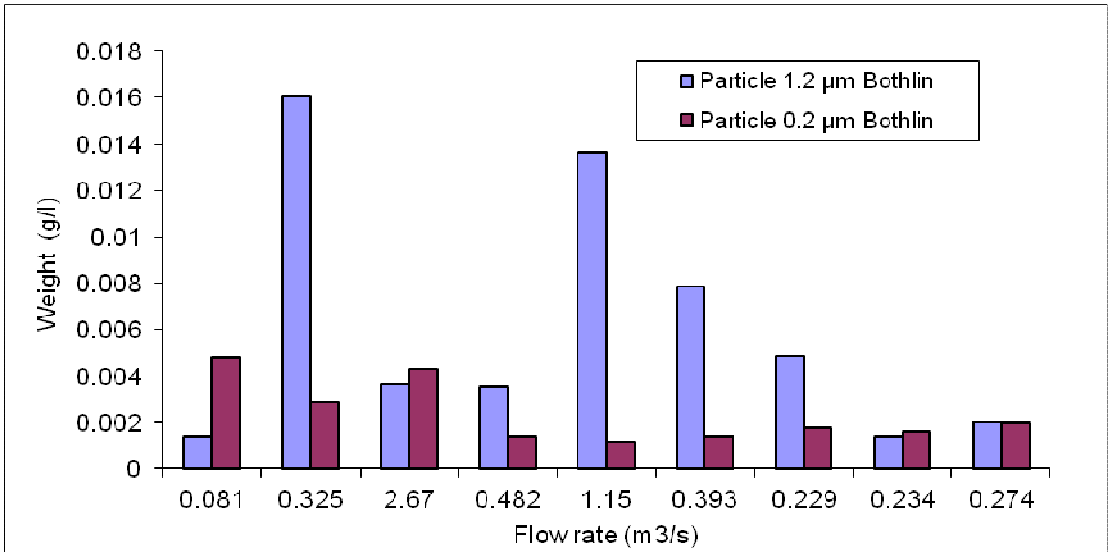

Figure 5- 9 Variation of mass of suspended sediment (g/ l) with flow rate of water for the > 1.2 µm and in the range 1.2 µm to 0.2 µm sediment from Bothlin Burn.

The mass of the suspended sediment with flow rate in the two size fractions is shown in Figure 5-10 and Figure 5-11 shows the variation of mass of suspended sediment with flow rate from Luggie Burn. There is no strong relationship between the flow rate and mass of sediment. In the > 1.2 µm fraction, high mass of sediment was measured with low flow rate. On the other hand, the mass of sediment was high with the flow rate in November 2009. The sediment mass in the > 1.2 µm fraction is high in July 2009 with low flow rate (0.322 m^3/s) and the sediment mass decreased in the following months. The sediment mass is similar in August in the two size fractions. The mass in the > 1.2 µm fraction was then increased in the next two sampling months, September (0.44 m^3/s) and in November 2009 (1.68 m^3/s). On the other hand, the mass of sediment in the range 1.2 - 0.2 µm diameters is higher than the sediment mass in the > 1.2 µm fraction in June 2009/2010, with low flow rate.

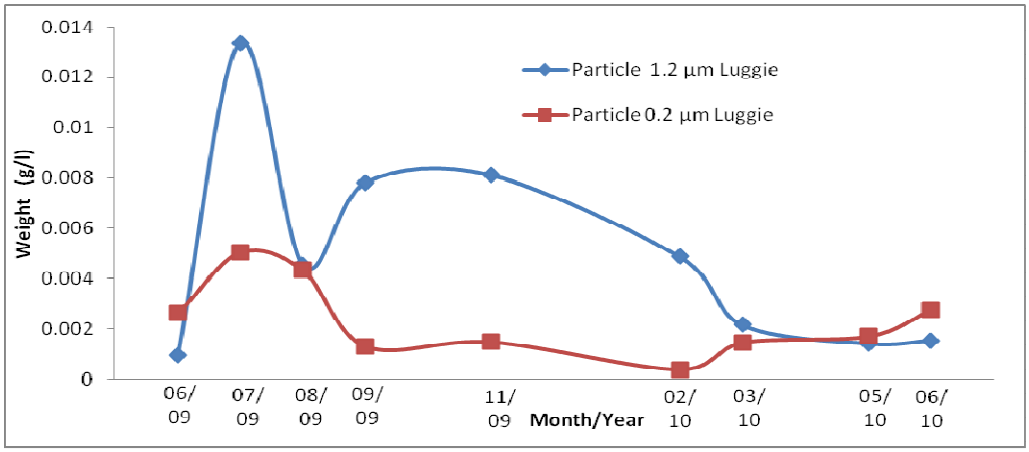

Figure 5- 10 Mass of suspended sediment (g/ l) water in the > 1.2 µm and in the range 1.2 µm to 0.2 µm from Luggie Burn.

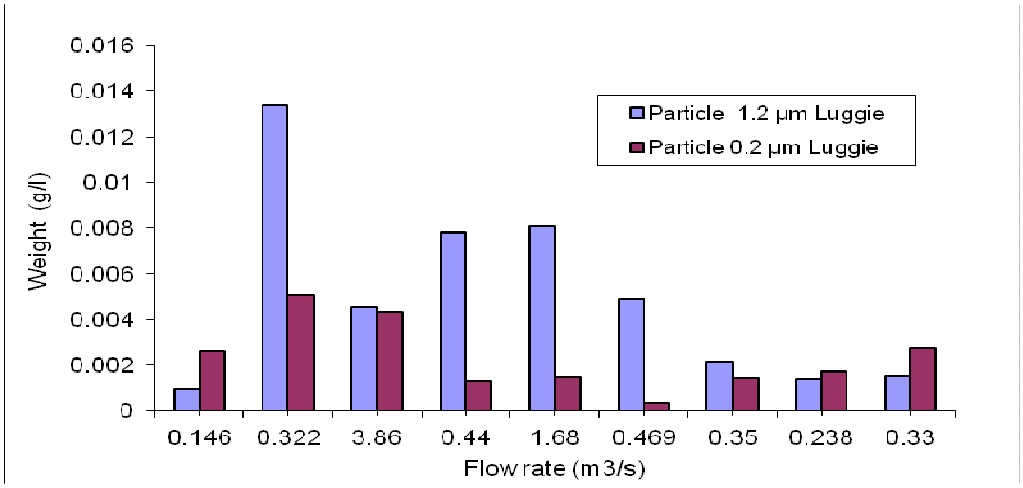

Figure 5- 11Variation of mass of suspended sediment (g/ l) with flow rate of water for the > 1.2 µm and in the range 1.2 µm to 0.2 µm sediment from Luggie Burn.

Figure 5-12 compares the sediment masses in the > 1.2 µm and sediment in the range 1.2 - 0.2 µm fractions, from Bothlin Burn and Luggie Burn, because the sampling sites are near to the point of the two tributaries coming together. The masses of the sediment in the > 1.2 µm fraction show a similar trend in the two tributaries. The mass of the larger fraction is similar in both rivers, where the higher mass measured in July and November 2009 with small divergence. In addition, the sediment mass in the 1.2 - 0.2 µm fractions is similar in both tributaries. The sediment mass in the 1.2 - 0.2 µm fractions was higher in summer 2009. After that the mass of sediment in the 1.2 - 0.2 µm fractions remained fairly constant in the rest of the sampling months. The increase and decrease of the mass of sediment for the two size fractions is similar in both tributaries.

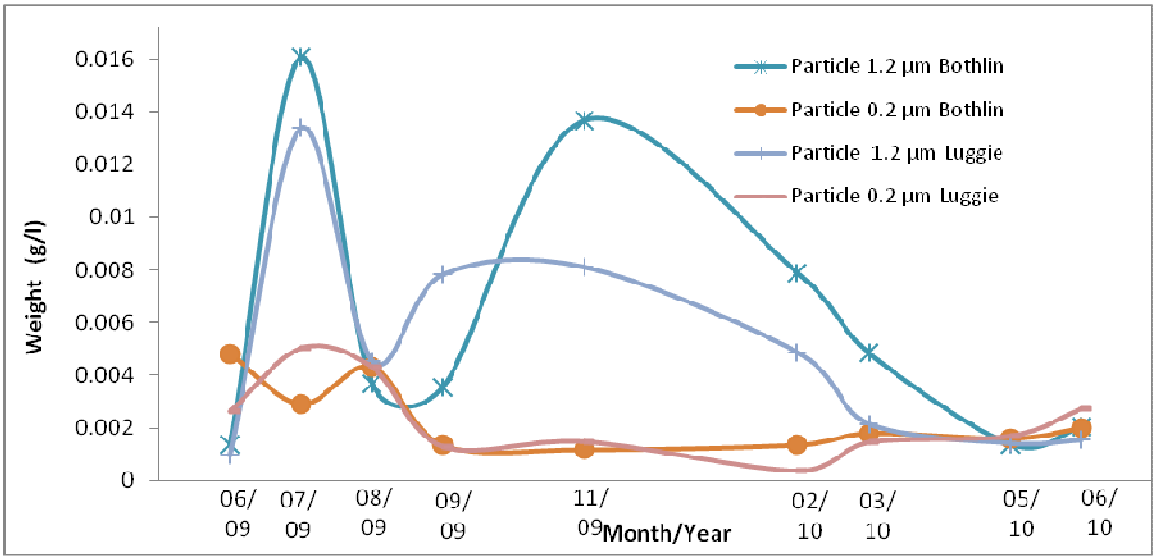

Figure 5- 12 Mass of suspended sediment (g/ l) water the > 1.2 µm and in the range 1.2 µm to 0.2 µm diameter size fractions from Bothlin Burn and Luggie Burn.

Figure 5-13 and Figure 5-14 show together the differences of the mass of sediment of two size fractions in the tributaries Craigmaddie Burn, Glazert Water, Bothlin Burn and Luggie Burn. The results demonstrate that the masses of the sediment in the > 1.2 µm fraction show a similar trend in the Craigmaddie Burn and Glazert Water and in the Bothlin Burn and Luggie Burn tributaries with small divergences. The mass of the sediment in the > 1.2 µm fraction is higher in July and November 2009. The trends of mass sediment are similar in Craigmaddie Burn and Glazert water. In addition, trends of mass of sediment are similar in the Bothlin Burn and in Luggie Burn, because the sampling sites are near to the point of the two tributaries coming together. The mass of sediment in the Bothlin Burn and in Luggie Burn was higher than the mass of sediment in Craigmaddie Burn and Glazert water. The mass was low in August 2009 and in the winter and summer sampling months 2010.

The results show that the masses of the sediment in the 1.2 µm to 0.2 µm fractions show a similar trend in the Craigmaddie Burn and Glazert Water and in the Bothlin Burn and Luggie Burn. In addition, the mass in the 1.2 µm to 0.2 µm fractions shows a similar trend in Bothlin Burn and Luggie Burn, and in the Craigmaddie Burn and Glazert water through the sampling months. The mass of the fine fraction is slightly increased in the summer of 2009 and decreased in the winter of 2009/10. The mass of the small fraction is higher than that in the large fraction in August in the two rivers Craigmaddie Burn and Glazert Water.

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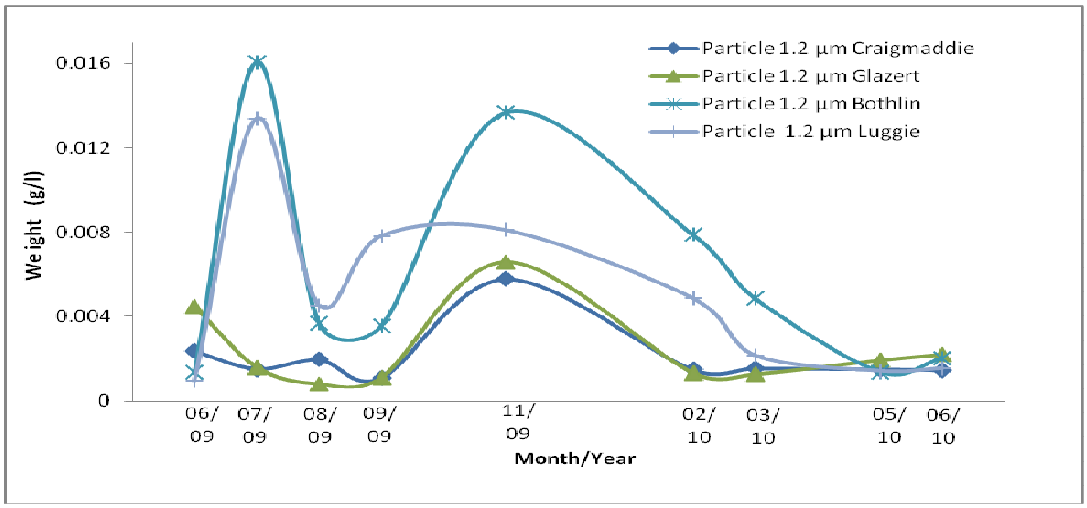

Figure 5- 13 Mass of suspended sediment (g/ l) in the > 1.2 µm diameter size fraction from Craigmaddie Burn, Glazert water, Bothlin Burn and Luggie Burn.

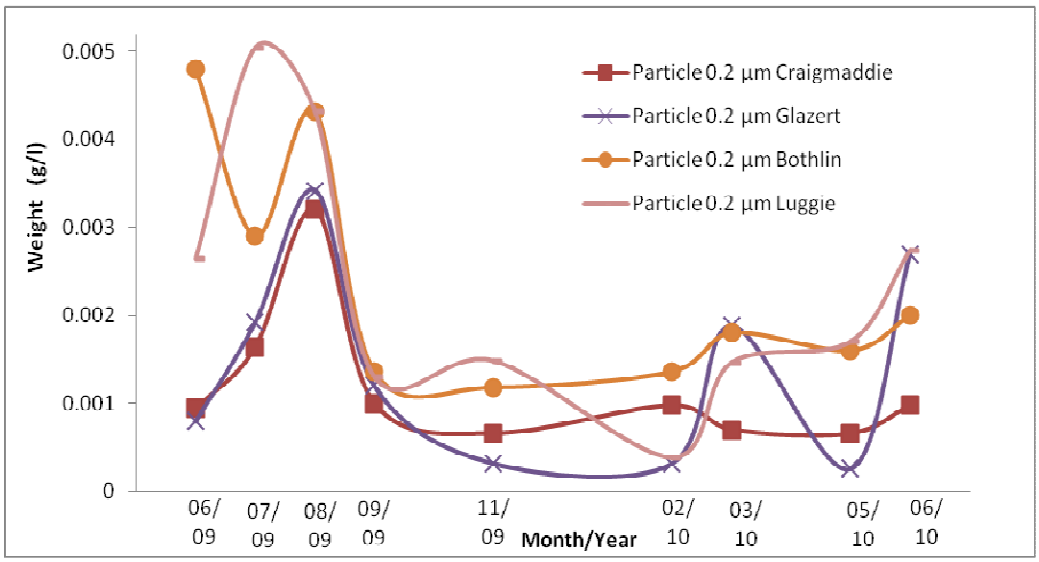

Figure 5- 14 Mass of suspended sediment (g/ l) in the 1.2 - 0.2 µm diameter size fraction from Craigmaddie Burn, Glazert water, Bothlin Burn and Luggie Burn.

The mass of the suspended sediment in the > 1.2 µm and sediment in the range 1.2 and 0.2 µm from Cameron Burn is shown in Figure 5-15. The sampling from Cameron Burn was undertaken on only five occasions, because of major highway construction within the sampling time and restricted access due to bad weather in the 2009/10 winter. The mass of the suspended sediment in the > 1.2 µm fraction is higher than the mass in the 1.2 - 0.2 µm fraction in September and November 2009. On the other hand, the mass of the sediment in the range 1.2 µm to 0.2 µm is higher than the sediment mass in the > 1.2 µm fraction in June, July and August.

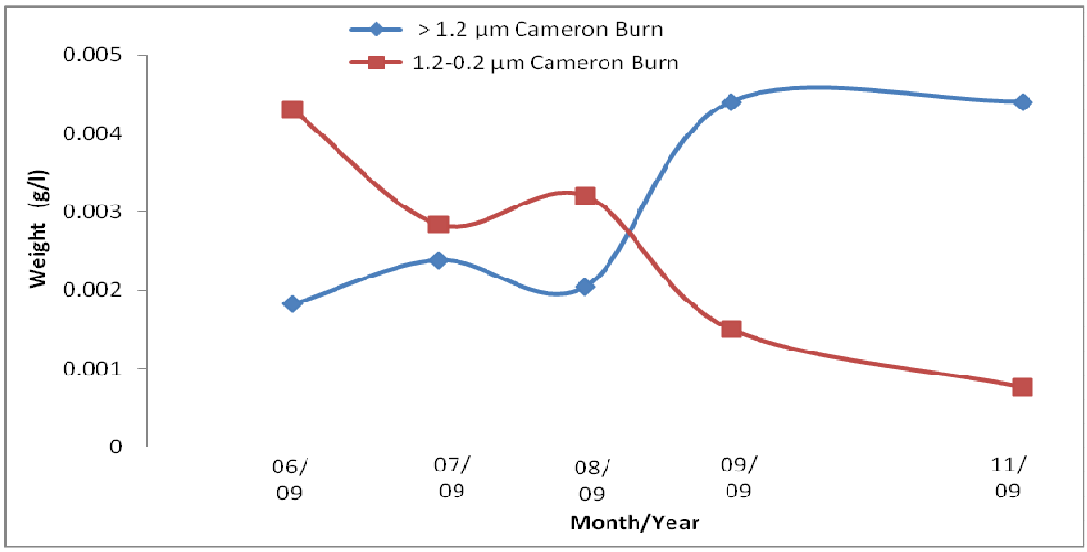

Figure 5- 15 Mass of suspended sediment in litre of water in the > 1.2 µm and 1.2 – 0.2 µm diameter size fractions from Cameron Burn (g/ l).

The mass of suspended sediment in the >1.2 µm fraction and in the 1.2 - 0.2 µm fraction from Cameron Burn near to land fill discharge are shown in Figure 5-16. The sediment mass in the >1.2 µm fraction was slightly higher than the mass of sediment in the 1.2 - 0.2 µm fraction in most sampling months, except in June 2009. The mass of the suspended sediment in the range 1.2 µm to 0.2 µm is higher than the mass in the > 1.2 µm fraction in June 2009. There is a steep decrease of the sediment mass in the 1.2 - 0.2 µm fraction in the rest of the sampling months.

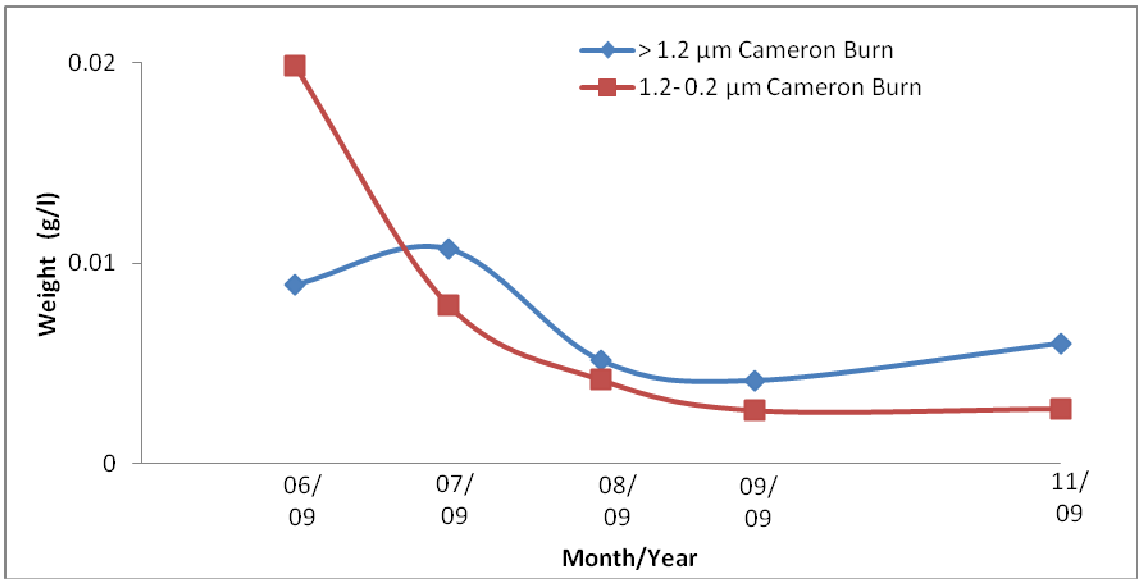

Figure 5- 16 Mass of suspended sediment (g/ l) in the > 1.2 µm and in the range 1.2 – 0.2 µm diameter size fractions near to land fill discharge to Cameron Burn.

5.1.1 Conclusion

The overall result indicated the mass of sediment was generally higher in the > 1.2 µm fraction than the fine particle fraction in the range 1.2 µm to 0.2 µm diameter. There is no strong association between the flow rate and mass of sediment. Where higher flow rate does not always cause increase in mass and lower flow rate does not always cause decrease in the mass of sediment. A high flow rate does not always mean a large mass of sediment transported. While decreased flow rate does not always mean a small sediment transport in the stream. The date of sampling may have an influence for the mass of sediment. For example, the Allander was sampled during a period of rising flow in November 2009, but decreasing flow in August 2009 (Table 5-2). Small changes in flow rate may affect the sedimentation of different particle sizes. In general the mass of sediment in the > 1.2 µm fraction is similar in most tributaries. The mass of sediment in the > 1.2 µm fraction was higher in July and November 2009. This may be due to the effect of rainfall amount, which can carry coarse sediment with high flow rate. In addition, the mass of the suspended sediment in the range 1.2 to 0.2 µm fraction was similar in most tributaries. The mass of sediment in the 1.2 to 0.2 µm fraction was higher in August 2009, February, March and May 2010. The overall mass of sediment in the two size fractions increased with increased flow rate, but in some cases the large particle deposited rapidly and the fine sediment dominated in the solution. In addition, some factors may be affecting the mass sediment in the solution such as the sampling time, flow rate before the sampling day, the rainfall seasons and the agricultural activity.

5.2 River Water Samples – metal concentrations in suspended sediment

Figures 5-17, 5-18 and 5-19 show the metal concentrations that were found in the > 1.2 µm fraction of the suspended sediment from Craigton Burn. Table 5-3 shows the metal concentrations varied over a wide range, such as Ca (81-296 mg/g) and Mg (10-161 mg/g).

Table 5- 3 Ranges of metal concentrations (mg/g) in the >1.2 µm and 1.2 - 0.2 µm diameter fractions of suspended sediment from Craigton Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	81.1–296	10.8–142	2.2-67.9	10.2-161	3.1–9.5	0.2–11.5
1.2 - 0.2 µm	9.6–72.5	13–58	1.6-18.2	1.6-21.5	0.3–2.1	0.3–6.1

The metal concentration trends over time are similar; the concentrations increased in summer and autumn 2009. Most of the element concentrations increased in August and November 2009. The Mn concentration increased in June and September 2009. The concentrations for Fe and Mg in November 2009 were the highest among the samples, while the lowest concentration (10.8 mg/g) for Fe was in July 2009 and for Mg was (10.2 mg/g) in May 2010. Concentrations for Ca, K and Zn in August 2009 were the highest among all samples. The lowest Ca, K and Zn concentrations were in June 2010 with increased mass of sediment. The metal concentration trends increased in summer and autumn (August and November 2009) and slightly decreased in winter 2010. In summer 2010 concentrations increased for Ca and Fe in May 2010, and concentrations increased for Mn in June 2010. The correlations between metals are shown in table 5-4. A positive correlation was observed between K and Ca ($P, < 0.01$) and to a lesser extent ($P, < 0.02$) between K and Zn.

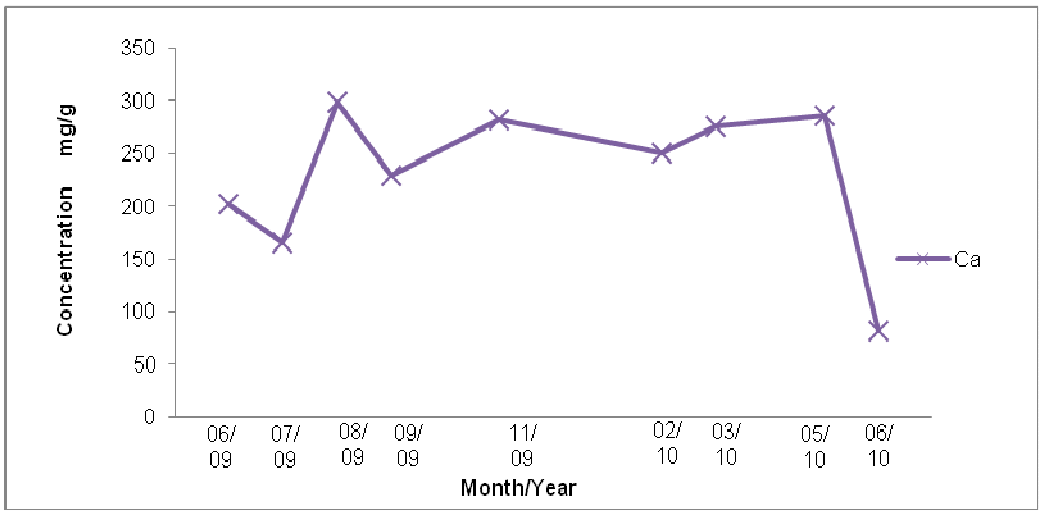

Figure 5- 17 Concentrations of Ca in suspended sediment (mg /g) of > 1.2 µm diameter from Craigton Burn.

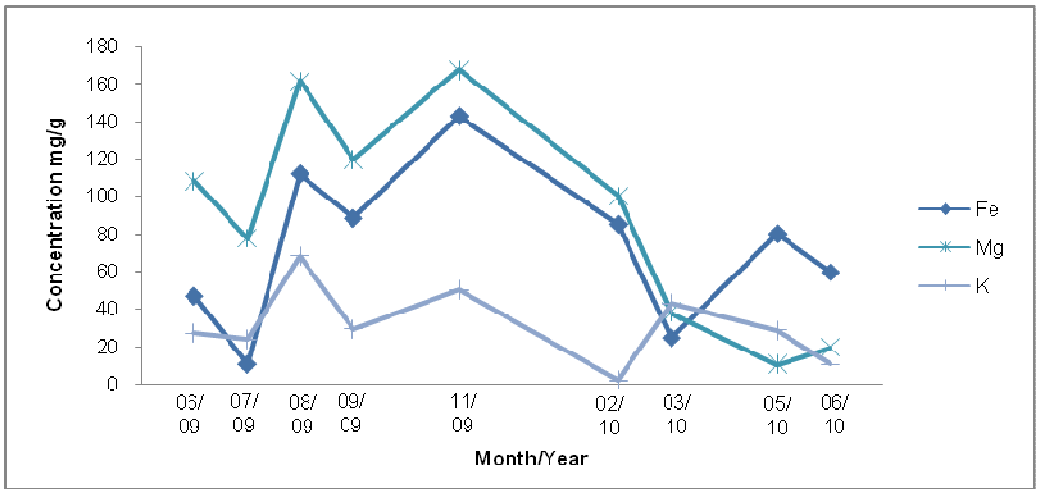

Figure 5- 18 Concentrations of Fe, K, and Mg in suspended sediment (mg /g) of > 1.2 µm diameter from Craigton Burn.

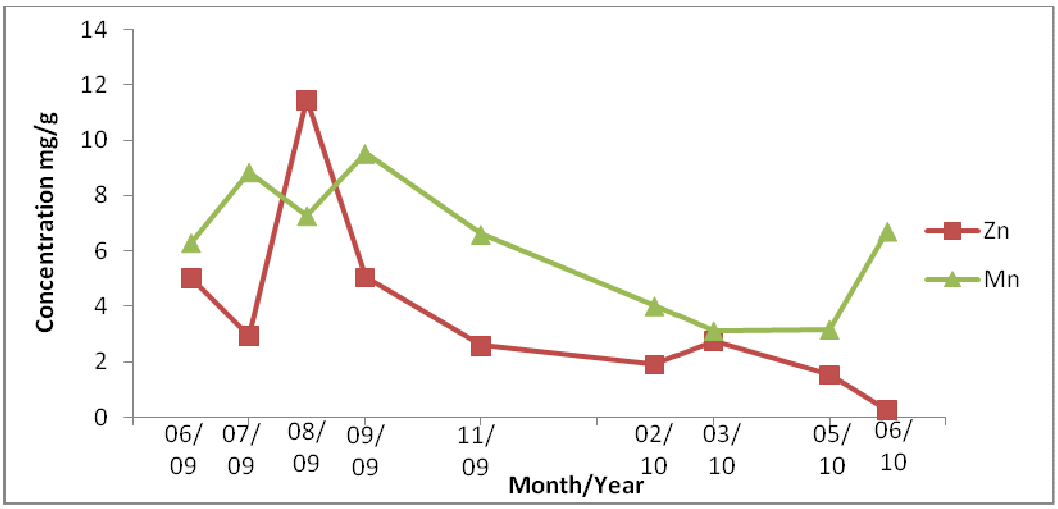

Figure 5- 19 Concentrations of Mn and Zn in suspended sediment (mg /g) of > 1.2 µm diameter from Craigton Burn.

Figures 5-20, 5-21, and 5-22 show the metal concentrations in the suspended sediment in the range 1.2 µm to 0.2 µm fraction from Craigton Burn. The concentration ranges are shown in table 5-3. The concentrations of the six metals show similar trends. Most of the concentrations were high in June, November 2009 and May 2010. All metals show concentration maxima in November 2009 and in May 2010, with lower levels in August 2009 and February and June 2010. The Zn concentration (0.2 mg/g) shows a low level in August 2009, while the concentration for Mn shows a lower level (3.1 mg/g) in February 2010. The concentrations for Ca, Fe, Mn, and Mg in November 2009 were the highest among the samples; while the lowest concentrations for Ca, Fe, Mn, and Mg were in February 2010. Concentrations for Ca, K and Zn in May 2010 were the highest among all the samples, and the lowest Ca, K and Zn concentrations were in August 2010. The correlations between metals are shown in table 5-5. A strong positive correlation was observed between Fe, Ca and Mg (P, < 0.005) and to a lesser extent (Pe, < 0.05) between Fe, K, Mn and Zn. A positive correlation also existed between Mn, Ca and Mg (P, < 0.05).

The data show that the average concentration in the nine sampling occasions display an overall trend. The metals concentration trend is to increase in summer and autumn 2009 and decrease in winter 2010, in the two particle size fractions used. As runoff increases and mass of sediment per liter of water decreases in the summer and autumn 2009, the concentrations are increased in these metals. Higher metal concentration was measured in August 2009 in the large particle size range. On the other hand, low metal concentration was measured in August 2009 in the 1.2 µm to 0.2 µm fraction, with a large mass of sediment. That may be due to high flow rate mobile particle containing elements not being determined in current study. While in November 2009 the metal concentration was higher in both size fractions with high flow rate. In addition, in May 2010 high metal concentration was observed in the fine particles. The highest concentrations for Fe and Mg in two fractions were measured in the same month November 2009 and for other metals the highest concentrations in the two fractions were measured in different months. Ca and Fe show similar trends in May 2010 in the two size fractions.

Overall the concentrations in the larger sediment >1.2 µm was higher than the concentration in the range 1.2 to 0.2 µm. The overall result indicated higher metal concentrations were measured in the > 1.2 µm fraction. On the other hand, low metal concentration was measured in the > 1.2 µm fraction with large sediment mass.

Table 5- 4 Correlations between concentrations of different metals in the 1.2 µm fraction from Craigton Burn

	Fe	Zn	Mn	Ca	Mg
Zn	0.292				
	0.446				
Mn	0.066	0.367			
	0.867	0.331			
Ca	0.560	0.523	-0.353		
	0.117	0.149	0.352		
Mg	0.622	0.657	0.491	0.406	
	0.074	0.055	0.180	0.278	
K	0.394	0.723	0.128	0.757	0.521
	0.294	0.028	0.743	0.018	0.150

Cell Contents: Pearson correlation
P-Value

Table 5- 5 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Craigton Burn

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.695				
	0.038				
Mn_1	0.762	0.205			
	0.017	0.596			
Ca_1	0.946	0.645	0.790		
	0.000	0.061	0.011		
Mg_1	0.905	0.405	0.876	0.820	
	0.001	0.280	0.002	0.007	
K_1	0.792	0.947	0.344	0.765	0.517
	0.011	0.000	0.365	0.016	0.154

Cell Contents: Pearson correlation
P-Value

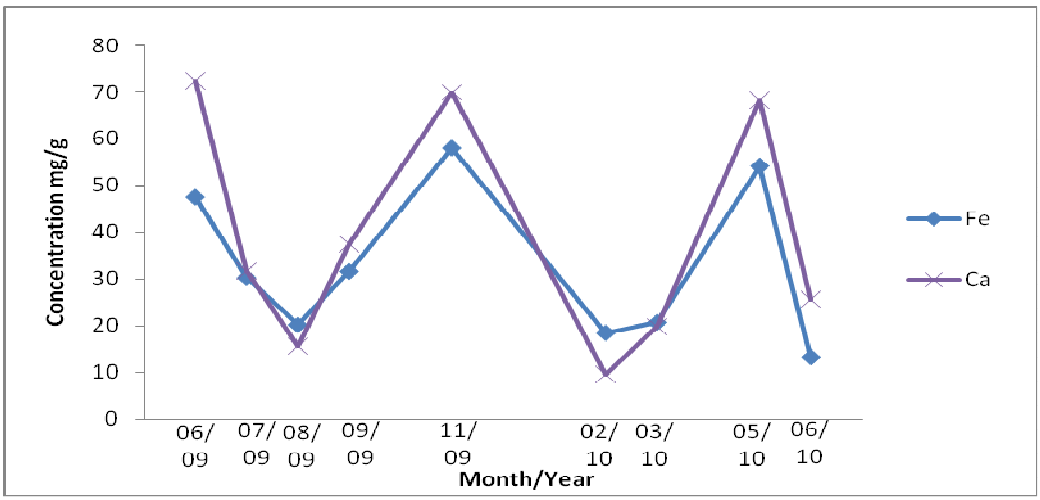

Figure 5- 20 Concentrations of Fe and Ca in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Craigton Burn.

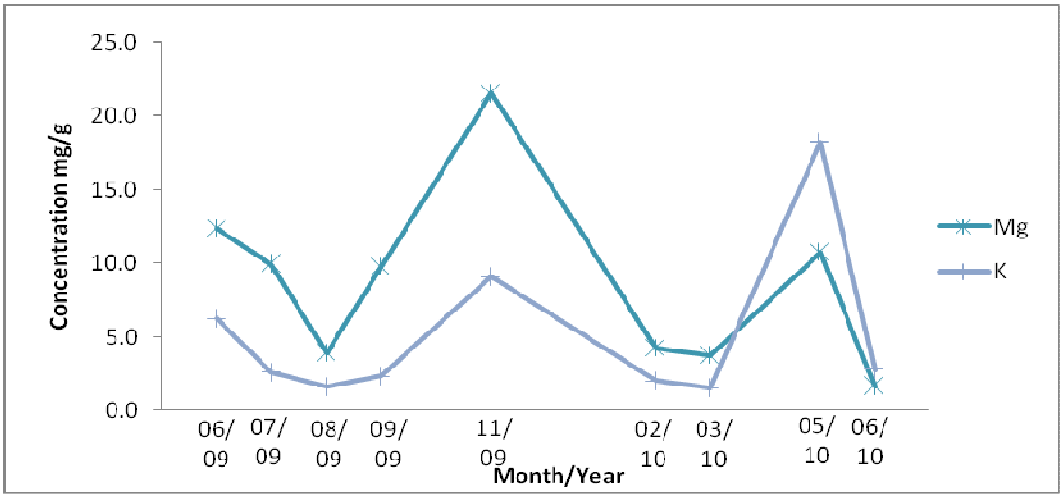

Figure 5- 21 Concentrations of K and Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Craigton Burn.

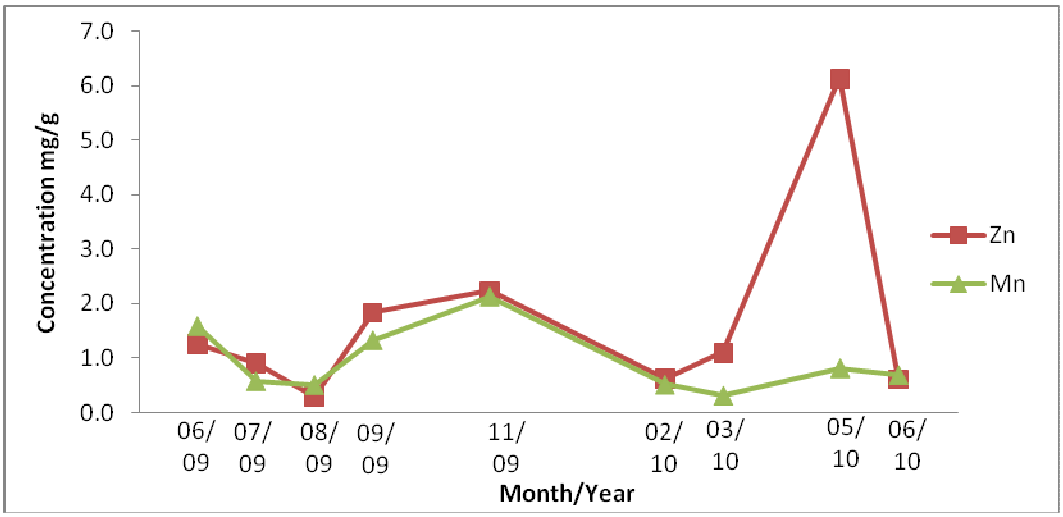

Figure 5- 22 Concentrations of Mn and Zn in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Craigton Burn.

The concentration ranges of metals in suspended particles in the > 1.2 µm fraction from Allander water are shown in table 5-6 and seasonal trends in Figures 5-23 and 5-24. The six metal concentrations show similar trends in summer 2009. The concentration increased in summer 2009 and decreased in winter 2010. All concentrations increased in July, August and September 2009. On the other hand, the concentrations for Ca and Mg increased in August, November 2009 and February 2010. The highest concentrations for Fe, Mn and Zn were measured in August and November 2009, which may be because high flow rate (4.01 m^3/s) increased the total of metal transport. The lowest metal concentrations were measured in June 2010 with low flow rate (0.11 m^3/s). The concentration trend is similar for Mn and Zn, where both increased in August 2009 with high flow rate and decreased in the rest of the sampling months. The result shows there is no strong association between the flow rate and the concentrations of metal in the suspended sediment because increasing the flow rate does not always cause an increase in the metals in the suspended sediment and low flow rate does not always cause a decrease in the metals in the suspended sediment. The concentrations of metal in suspended sediment in the > 1.2 µm fraction from Allander water and Craigton Burn shows similar trends. Table 5-7 shows a strong positive correlation was observed between Fe and Mn (P, < 0.007) and Positive correlation was observed Ca and K (P, < 0.005). A lesser extent (P, < 0.03) between Fe and Zn. Positive correlation also existed between Zn, and Mn (P, < 0.01).

Table 5- 6 Ranges of metal concentrations (mg/g) in the>1.2 µm and 1.2-0.2 µm diameter suspended sediment from Allander Water

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	22.3–297	37–163	9.8-66	3.7-282	1.6–12.1	0.1–8.9
1.2 - 0.2 µm	15.6-137	11–139	0.7-30.8	3.4-37.5	0.2–9.4	0.3–8

Figures 5-25, 5-26, and 5-27 show the concentrations of metals in the suspended sediment in the size range 1.2 µm to 0.2 µm. The concentrations of most of the metals show similar trends. The concentrations increased in summer, autumn 2009 and summer 2010. The concentration ranges for Ca, Fe, K, Mg, Mn and Zn in the suspended sediment are shown in table 5-3. All concentrations increased in the autumn of 2009 and winter of 2010 and decreased in the summers of 2009 and 2010. The higher metal concentrations were measured in July with low flow rate (0.11 m^3/s), also in February 2010 with low flow rate (0.371 m^3/s). In November 2009 the concentrations were higher with high flow rate (2.19 m^3/s). In addition, there were slight increases of the metal concentrations in July 2009 and June 2010. Concentrations for Ca, Fe, K and Mg in November were the highest, which may be due to high flow rate (2.19 m^3/s) increasing the total metals. The lowest Ca, Fe, K and Mg concentrations were measured in August 2009. This may be a result of increase flow rate carry material which containing elements not specified in the current study. Concentration of Zn was the highest in February 2010 (8 mg/g) and lowest Zn in August 2009 (0.3 mg/g). The concentrations of metal in suspended sediment in the 1.2 µm to 0.2 µm fraction from Allander water and Craigton Burn show similar trends, with small divergences. In the Allander Burn there are some correlations between concentrations of different metals in the particle range 1.2 and 0.2 µm as shown in table 5-8. A strong positive correlation was observed between Fe, Mg, Ca and Mn ($P, < 0.005$) and to a lesser extent ($P, < 0.05$) between Fe and Zn. Positive correlation also existed between Zn, Ca and Mg ($P, < 0.005$). Positive correlation was observed Mn, Ca and Mg ($P, < 0.05$).

Table 5-7 Correlations between concentrations of different metals in the 1.2 µm fraction from Allander Water

	Fe	Zn	Mn	Ca	Mg
Zn	0.702				
	0.035				
Mn	0.819	0.788			
	0.007	0.012			
Ca	0.462	0.345	0.171		
	0.211	0.363	0.661		
Mg	0.494	0.323	0.387	0.739	
	0.177	0.396	0.304	0.023	
K	0.345	0.562	0.157	0.836	0.516
	0.364	0.115	0.686	0.005	0.155

Cell Contents: Pearson correlation
P-Value

Table 5- 8 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Allander Water

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.757				
	0.018				
Mn_1	0.872	0.430			
	0.002	0.248			
Ca_1	0.912	0.882	0.683		
	0.001	0.002	0.043		
Mg_1	0.952	0.856	0.744	0.921	
	0.000	0.003	0.021	0.000	
K_1	0.518	0.445	0.423	0.551	0.406
	0.153	0.230	0.257	0.124	0.279

Cell Contents: Pearson correlation
P-Value

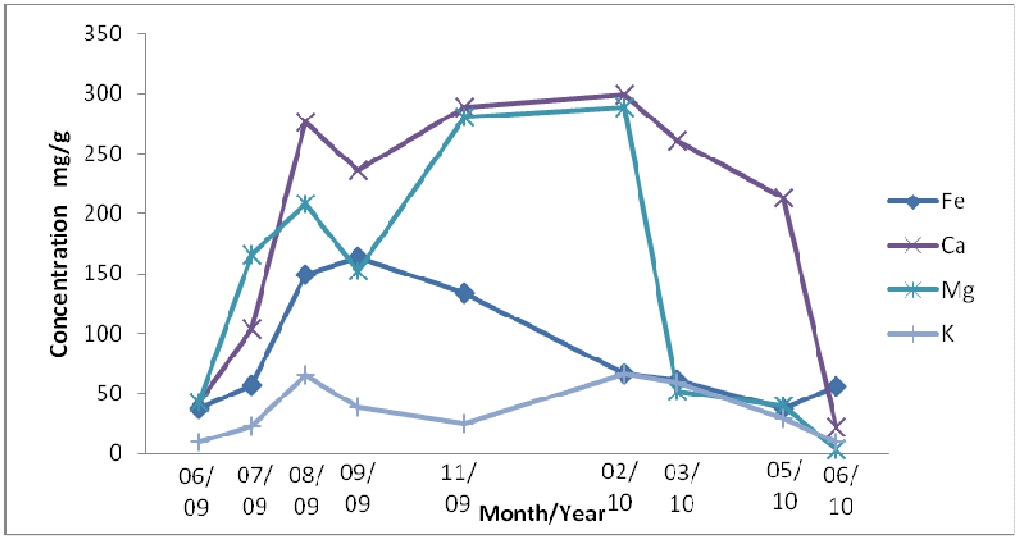

Figure 5- 23 Concentrations of Ca, Fe, K, and Mg in suspended sediment (mg /g) of > 1.2 µm diameter from Allander Water.

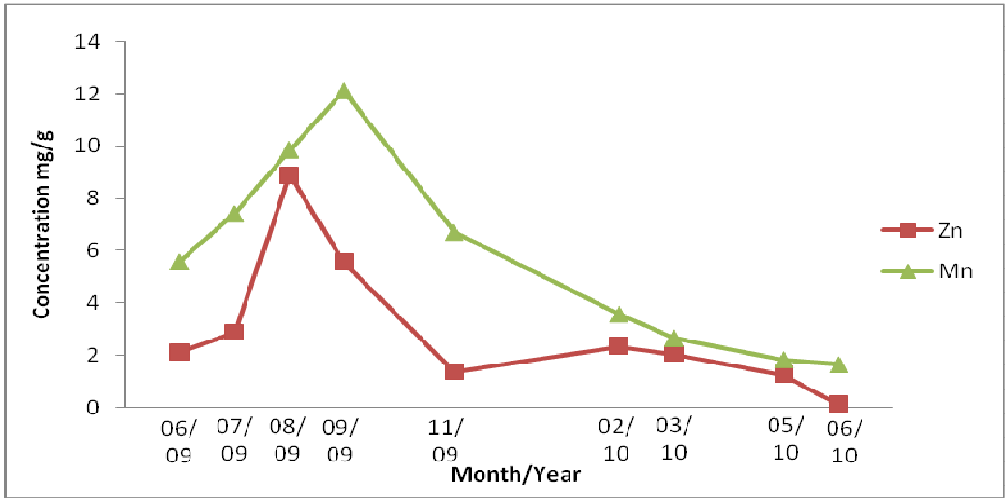

Figure 5- 24 Concentrations of Mn, and Zn in suspended sediment (mg/g) of > 1.2 µm diameter from Allander Water.

Most concentrations increased in summer 2009 and decreased in winter and summer 2010 for the >1.2 µm fraction. Ca and Mg concentrations increased in the summer 2009 and winter of 2010 and decreased in summer of 2010. In the 1.2 to 0.2-µm fraction the concentrations increased in autumn 2009 and winter 2010 and decreased in summer 2009 and 2010. The concentration in the sediment larger than 1.2 µm was higher than the concentration in the range 1.2 to 0.2 µm.

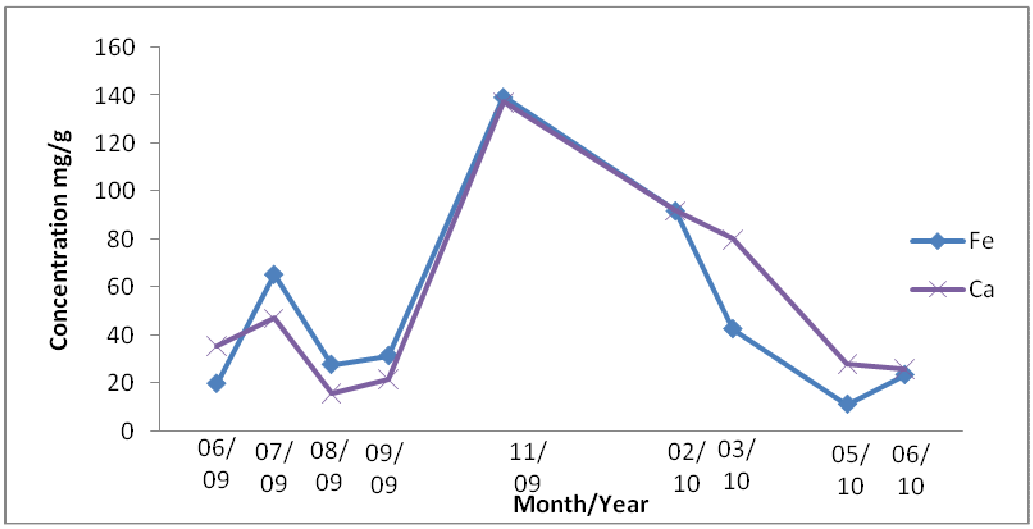

Figure 5- 25 Concentrations of Fe and Ca in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Allander Water.

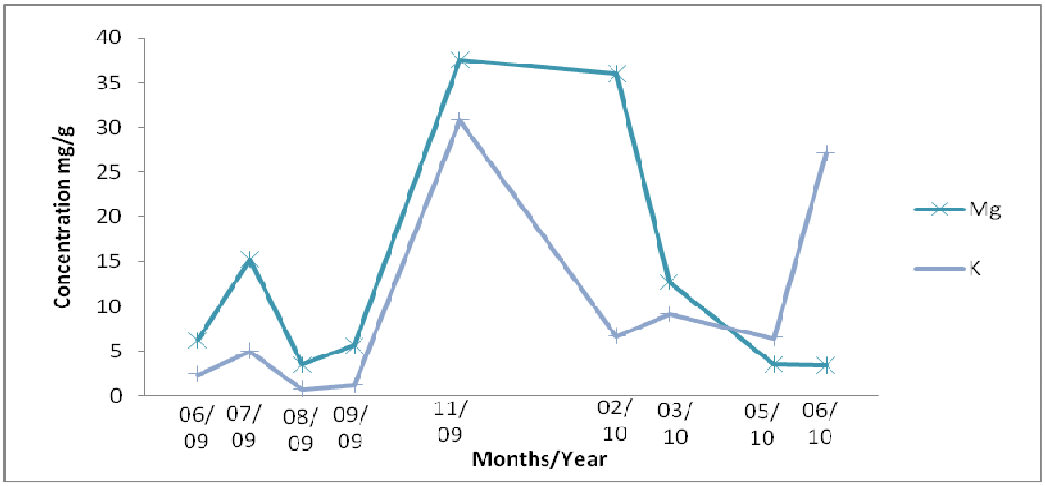

Figure 5- 26 Concentrations of K, and Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Allander Water.

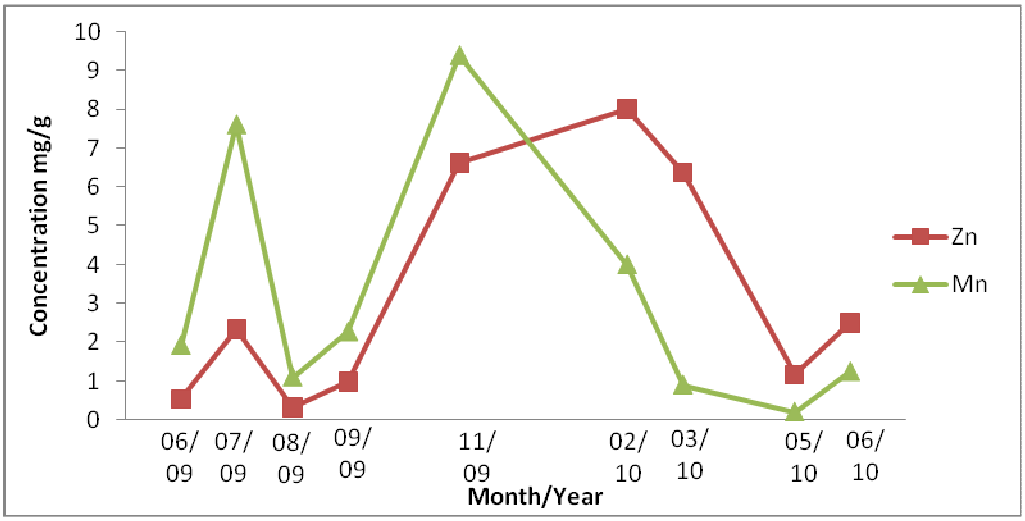

Figure 5- 27 Concentrations of Mn and Zn in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Allander Water.

Figures 5-28 and 5-29 show the seasonal trends in the concentrations of the six metals in samples from Craigmaddie Burn. The concentration ranges of metals in the suspended sediment in the > 1.2 µm fraction from Craigmaddie Burn are shown in Table 5-9. The figures show that the trends for metal concentrations are similar. The concentration increased in summer of 2009 and decreased in the autumn of 2009, after that the concentrations increased in winter of 2010 for most of the metals. The high concentrations were measured in the > 1.2 µm fraction in July, September 2009, March and June 2010. In contrast, the concentration of metal decreases with increased mass of sediment in August, November 2009. This may be due to the dilution by high flow rate which increases materials containing elements not being measured in this study. The maximum concentrations for Ca, Fe, K and Mg were shown in June 2009 and in September 2009 for Fe and Mn. The concentration increases in February 2010 for Mg and Mn, in March 2010 for Ca, Fe and K. In addition, all the metals show lower levels in November 2009 and in June 2010, with large sediment mass. The highest concentration for Ca was measured in March 2010; and the lowest concentration was measured in November 2009. Table 5- 10 shows a strong positive correlation was observed between Mn and Fe (P, < 0.002) and to a lesser extent (P, < 0.006) Mn and Zn. A strong positive correlation also existed between Ca and K (P, < 0.001).

Table 5- 9 Ranges of metal concentrations (mg/g) in the > 1.2 µm diameter in suspended sediment from Craigmaddie Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	29–249	40–223	1.7-42.5	13-230	2.37–15	0.48–4
1.2 - 0.2 µm	2.3–60.6	2.2–102	0.1-6.1	0.3-13.1	0.1–3.7	0.6–2.9

The concentration ranges of metals in the suspended sediment are shown in table 5-9. Figures 5-30, 5-31, and 5-32 show the concentrations of metals in the suspended sediment in the 1.2 µm -0.2 µm fraction from Craigmaddie Burn. The metal concentration trends are similar; the figures show concentrations of metals were increased in July, November 2009 and February 2010, and decreased in the summer of 2010. All concentrations in the 1.2 µm -0.2 µm fraction are increased from September 2009 until February 2010. The level of metal concentrations in summer 2010 are lower than average in June and July 2009.

The figure shows the average concentration of the nine occasions of results to exhibit an overall trend. There is metal correlation from Craigmaddie Burn in the data sets in table 5-11; Ca, Fe, and Mg and Mn were highly and positively correlated. A strong positive correlation was observed between Fe, Ca and Mg (P, < 0.005) and to a lesser extent (P, < 0.05) Fe, Mn and Zn. Positive correlation also existed between Zn, Ca and Mg (P, < 0.005). Positive correlation was observed Mn, Ca and Mg (P, < 0.005).

Table 5-10 Correlations between concentrations of different metals in the 1.2 µm fraction from Craigmaddie Burn

	Fe	Zn	Mn	Ca	Mg
Zn	0.374				
	0.127				
Mn	0.672	0.622			
	0.002	0.006			
Ca	0.317	0.333	0.039		
	0.201	0.176	0.878		
Mg	0.333	0.427	0.321	0.610	
	0.177	0.077	0.193	0.007	
K	-0.012	-0.052	-0.422	0.788	0.279
	0.962	0.837	0.081	0.000	0.262

Cell Contents: Pearson correlation
P-Value

Table 5-11 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Criagmaddie Burn

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.624				
	0.006				
Mn_1	0.629	0.436			
	0.005	0.070			
Ca_1	0.789	0.879	0.664		
	0.000	0.000	0.003		
Mg_1	0.784	0.851	0.723	0.895	
	0.000	0.000	0.001	0.000	
K_1	0.410	0.541	0.441	0.602	0.484

Cell Contents: Pearson correlation
P-Value

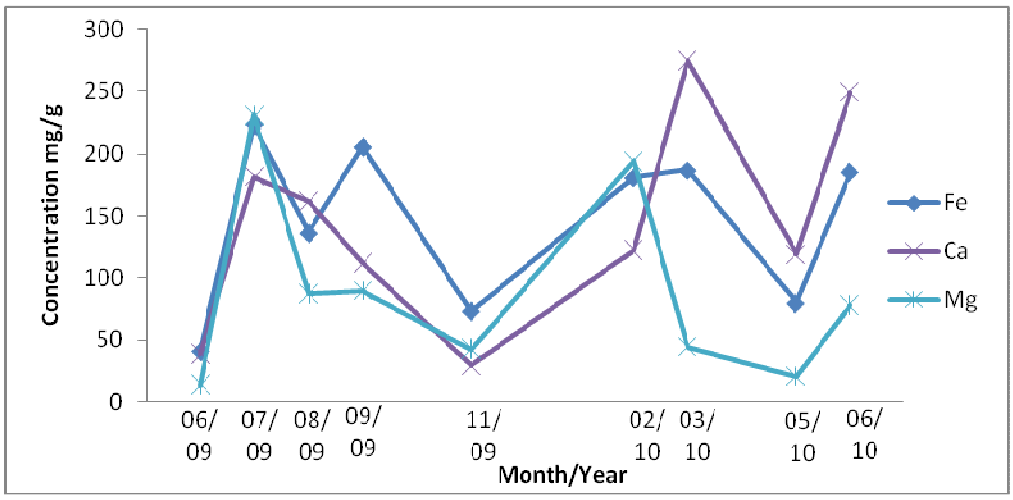

Figure 5- 28 Concentrations of Fe, Ca, and Mg in suspended sediment (mg/g) of > 1.2 µm diameter from Craigmaddie Burn.

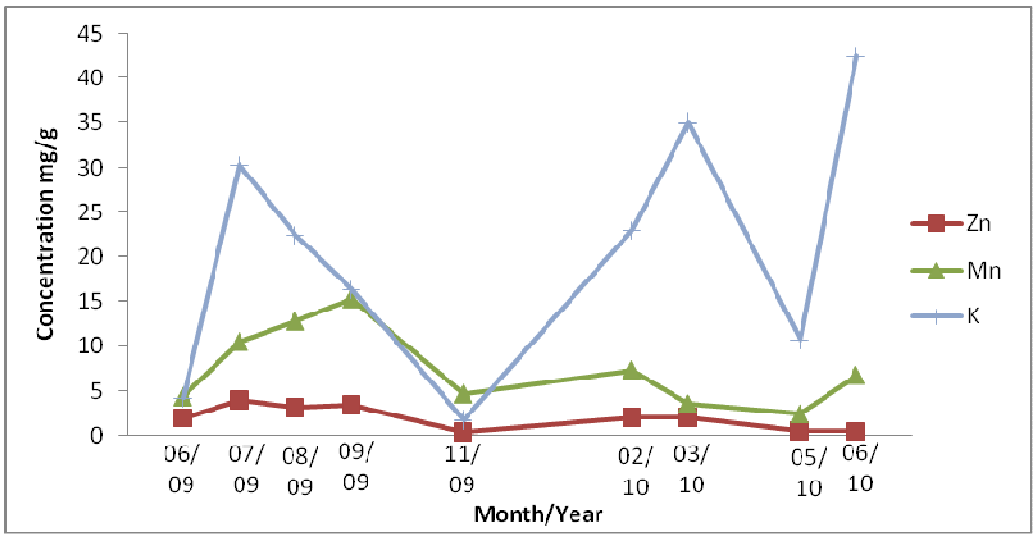

Figure 5- 29 Concentrations of K, Mn, and Zn in suspended sediment (mg /g) of > 1.2 µm diameter from Craigmaddie Burn.

The overall concentration trend over time was similar with the sediment size fraction used. The metal concentrations in the > 1.2 µm fraction are higher than the concentrations in the 1.2-0.2 µm fraction in the summer of 2009 and winter of 2010; while the concentrations in the 1.2-0.2 µm fraction were higher than the concentrations in the 1.2-0.2 µm fraction in autumn 2009 and winter 2010 and lower in the summers of 2009 and 2010. The metal concentration in the >1.2 µm was higher than the metal concentration in the size range 1.2 to 0.2 µm fraction.

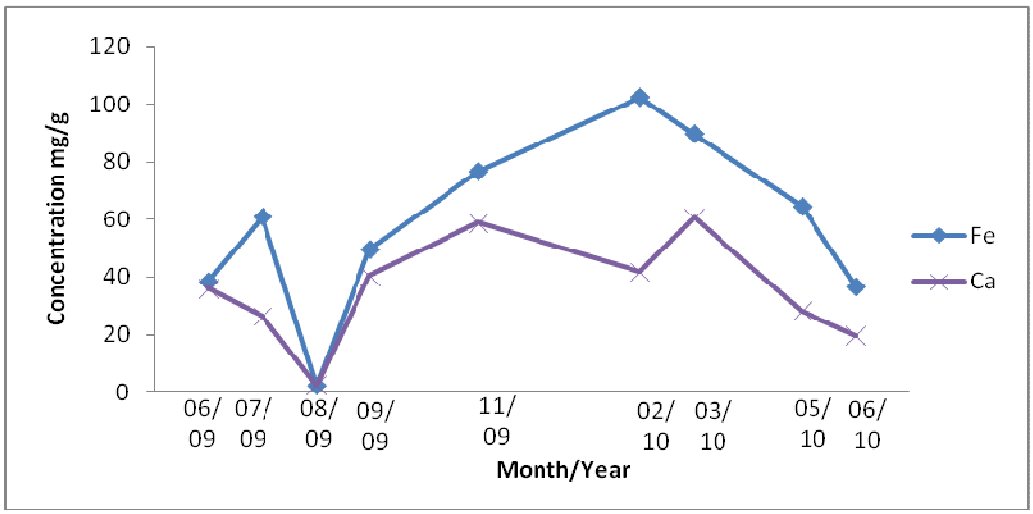

Figure 5- 30 Concentrations of Fe and Ca in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Craigmaddie Burn.

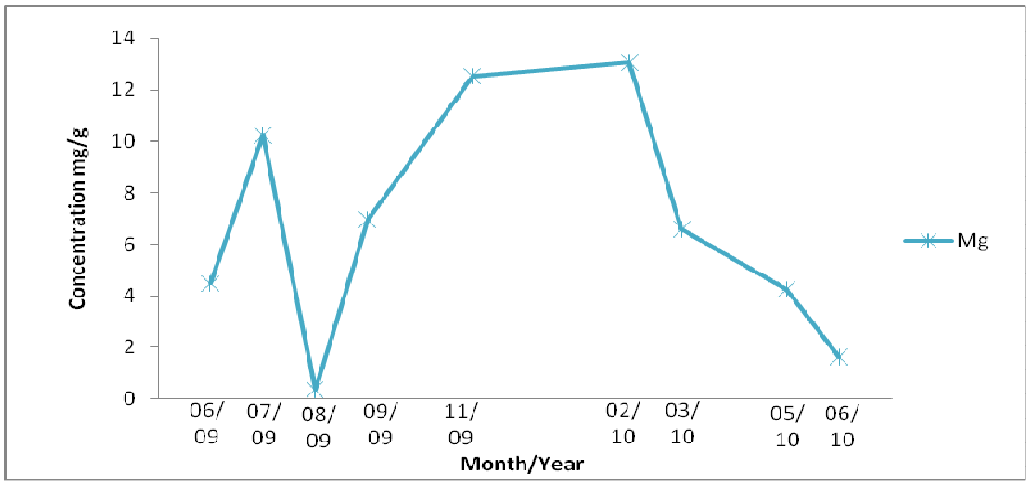

Figure 5- 31 Concentrations of Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Craigmaddie Burn.

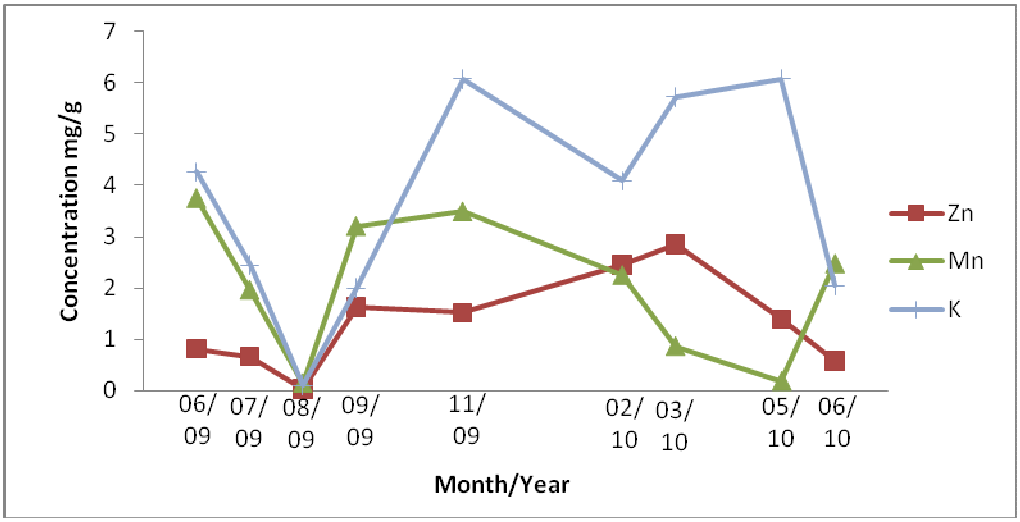

Figure 5- 32 Concentrations of K, Mn, and Zn in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Craigmaddie Burn.

Figures 5-33 and 5-34 show the concentrations in the suspended sediment in the > 1.2 µm fraction from Glazert water and concentration ranges of the metals in the suspended sediment are shown in table 5-12. The metal concentration trends are similar; the concentrations were higher in summer 2009/2010 with higher flow rate and in winter 2010 with low flow rate. The concentrations are higher in summer 2009 in July for Mg (263 mg/g) with high flow rate (1.32 m^3/s), in August for Ca, K and Zn with high flow rate (6.79 m^3/s), also in September for Fe and Mn with slight increase in flow rate (0.664 m^3/s). In addition, concentrations are higher in February 2010 with flow rate (0.562 m^3/s) and in June 2010 with low flow rate (0.274 m^3/s) for Ca, Fe, K and Mg. The concentration trends over time are similar for Ca, and K. On the other hand, metal concentrations are lower in June, with normal flow rate and in November 2009, with increased sediment mass with high flow rate (4.32 m^3/s). That may be because high flow rate carries a lot of materials are not determined in this study such as of quartz and other materials. The overall concentration trend is similar between the six metals throughout the nine sampling occasions. The concentrations of metal in suspended sediment in the 1.2 µm to 0.2 µm fraction from Craigmaddie Burn and Glazert water Burn shows similar trends. Table 5-13 shows a strong positive correlation was observed between Ca and K (P, < 0.001) and to a lesser extent (P, < 0.006) Mg and K. Positive correlation also existed between Ca and Mg (P, < 0.01).

Table 5-12 Ranges of metal concentrations (mg/g) in the > 1.2 µm and 1.2 - 0.2 µm diameter suspended sediment from Glazert Water

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	14–287	20–268	2.1-36.4	4.8-263	0.7–20.8	0.1–6.6
1.2 - 0.2 µm	9.8–101	8.7–290	0.6-7.7	1.6-35.6	1.8–52.4	0.1–6.2

Concentration ranges of metals in the suspended sediment in the range 1.2 to 0.2 µm from Glazert Burn are shown in table 5-12, and seasonal trends in Figures 5-35 to 5-37. The concentration trends over time are similar for increase and decrease for different elements throughout the nine sampling occasions. The concentrations were high with low flow rate in June 2009 and February and May 2010. The concentrations were high for Ca, Fe, K and Mg in February 2010 with flow rate (0.562 m^3/s) and in May 2010 with low flow rate (0.290 m^3/s). In addition, concentrations for Ca, K and Zn are higher in November 2009, in high flow rate (4.32 m^3/s). The highest concentrations for Ca, Fe, K, Mn, and Zn were measured in May 2010 and the lowest concentrations for Ca, Fe, K, Mn, and Zn were noted in August 2009 with high flow rate (6.79 m^3/s). Concentration of Mg (35.6 mg/g) in February 2010 was the greatest among all the months, and the lowest Mg (1.6 mg/g) concentration was measured in August 2009. The concentration trends over time are similar for the six metals throughout the nine sampling occasions. The results show there is no strong association in the 1.2 µm fraction and in the 1.2 to 0.2 µm fraction between the flow rate and the concentrations of metal in the suspended sediment. Increasing the flow rate does not always cause an increase in the metal in the suspended sediment, such as in August and November 2009, and low flow rate does not always cause a decrease in the metal in the suspended sediment, such as in February and June 2010. There are strong correlations between metals as shown in table 5-14. In the data sets Ca, Fe, and Mn were highly and positively correlated. Positive correlation was observed between Fe, Ca and Mn ($P, < 0.05$). A lower correlation was observed between Ca, Mg and K ($P, < 0.01$). Positive correlation also existed between Zn and Mn ($P, < 0.005$). Correlation was observed ($P, < 0.01$) between Ca and all other metals.

Table 5-13 Correlations between concentrations of different metals in the 1.2 µm fraction from Glazert Water

	Fe	Zn	Mn	Ca	Mg
Zn	0.242				
	0.530				
Mn	0.663	0.337			
	0.052	0.376			
Ca	0.581	0.508	0.119		
	0.101	0.163	0.760		
Mg	0.125	0.613	0.052	0.798	
	0.748	0.079	0.895	0.010	
K	0.301	0.643	-0.028	0.911	0.838
	0.432	0.062	0.942	0.001	0.005

Cell Contents: Pearson correlation
P-Value

Table 5-14 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Glazert Water

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.729				
	0.026				
Mn_1	0.884	0.823			
	0.002	0.006			
Ca_1	0.774	0.767	0.753		
	0.014	0.016	0.019		
Mg_1	0.511	0.648	0.374	0.796	
	0.160	0.059	0.321	0.010	
K_1	0.476	0.600	0.470	0.769	0.562
	0.195	0.088	0.201	0.015	0.115

Cell Contents: Pearson correlation
P-Value

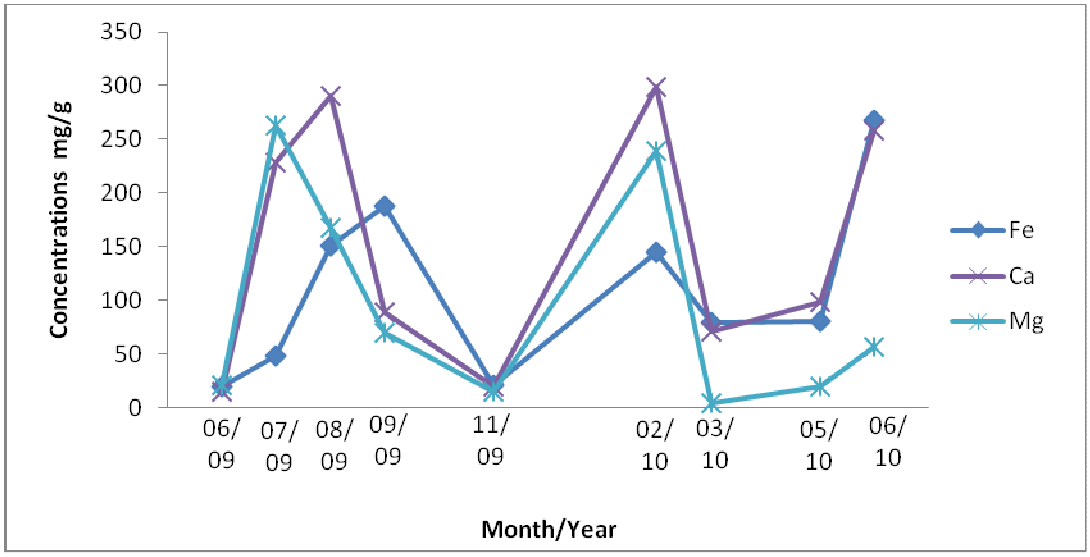

Figure 5- 33 Concentrations of Fe, Ca, and Mg in suspended sediment (mg /g) of > 1.2 µm diameter from Glazert Water.

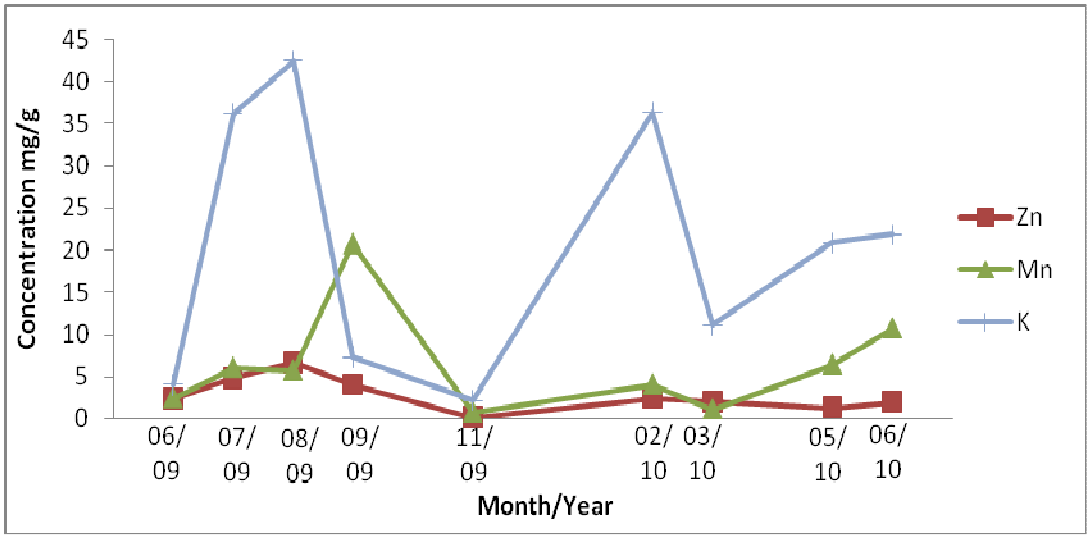

Figure 5- 34 Concentrations of K, Mn and Zn in suspended sediment (mg /g) of > 1.2 µm diameter from Glazert Water.

The concentration trends are similar throughout the nine sampling occasions in the two size fractions. The concentrations in the large particles increase in summer 2009 in September 2009 and in June 2010. On the other hand, the concentrations increase in the range 1.2 to 0.2 µm for Ca, Fe, K and Mg in February 2010 and in May 2010.

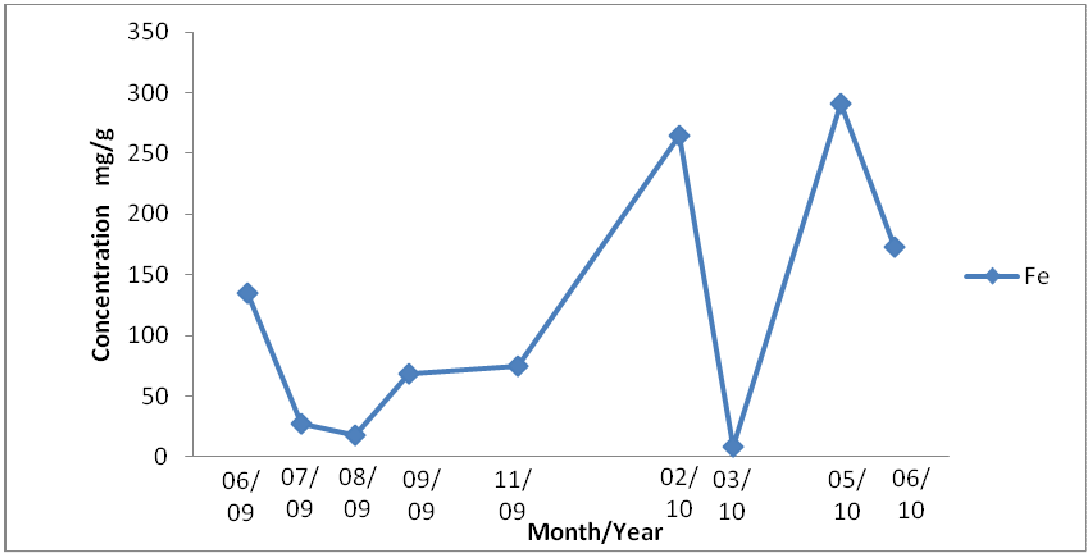

Figure 5- 35 Concentrations of Fe in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Glazert Water.

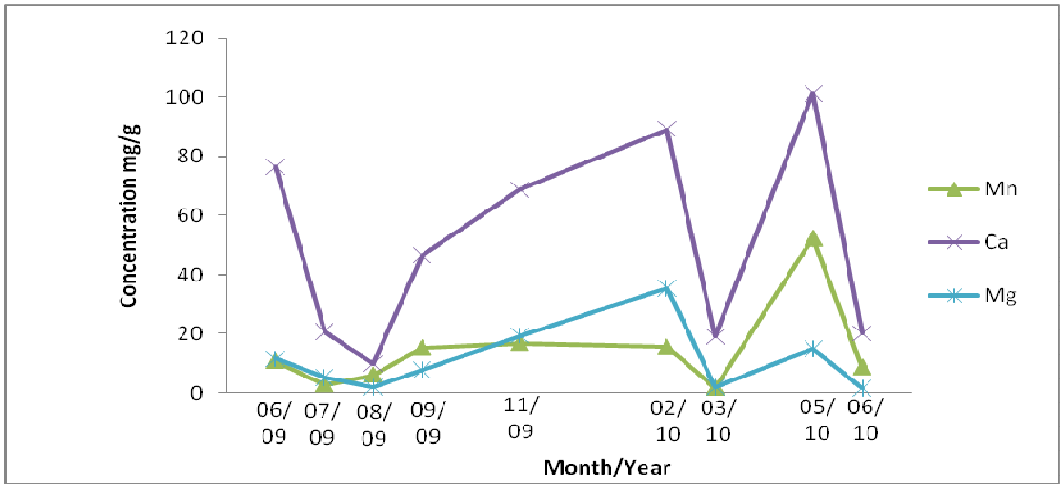

Figure 5- 36 Concentrations of Ca, Mg, and Mn in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Glazert Water.

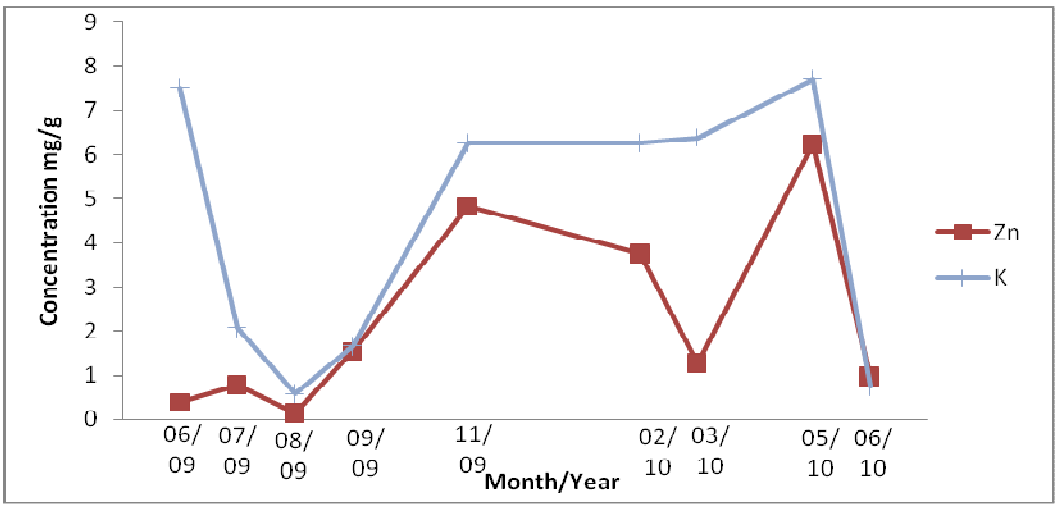

Figure 5- 37 Concentrations of K, and Zn in suspended sediment (mg /g) of (1.2- 0.2 µm) diameter from Glazert Water.

Figures 5-38, 5-39, and 5-40 show the concentrations of metals in the > 1.2 µm fraction from Bothlin Burn. The concentration ranges in the suspended sediment are shown in table 5-15. The metal concentration trends are similar, where the concentration increases with high flow rate in August 2009 and in February and May with low flow rate. All concentrations were higher at the start of the sampling campaign in June and August 2009. On the other hand, low metal concentrations were measured with high flow rate in November 2009, which maybe because high flow rate increased a lot of material, this materials containing elements not being measured. The concentration increased for Ca and Mg in February 2010 with low flow rate (0.393 m^3/s) and decreased in summer 2010. While for Fe and Mn the concentrations increased in May and June 2010 with low flow rate. The concentration for Ca, Fe, K and Zn was the greatest among the samples in August 2009 with high flow rate (2.67 m^3/s), while the concentrations for Ca, Fe, K and Zn were the lowest among the months in July 2009, with low flow rate (0.325 m^3/s). The concentrations increased for K, Mn and Zn metals in summer 2009, and decreased in winter 2010. On the other hand, the concentration for Ca, Fe, and Mg increased during summer 2009 and in winter 2010. Table 5- 16 shows positive correlation was observed between Fe and Mn (P, < 0.03), Fe and Ca (P, < 0.04) and Fe and K (P, < 0.01). A correlation was observed between K and Ca (P, < 0.01).

Table 5-15 Ranges of metal concentrations (mg/g) in the > 1.2 µm and 1.2 - 0.2 µm diameter suspended sediment from Bothlin Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	32–283	29–127	1.7-39.1	10.6-85	1.1–13.7	0.2–3.6
1.2 - 0.2 µm	32–104	12–154	0.9-7	3.8-22.2	0.2–3.5	0.3–2.1

The concentration ranges of Ca, Fe, K, Mg, Mn, and Zn in the suspended sediment are shown in table 5-15. Figures 5-41, 5-42, and 5-43 show the concentrations of metals in the suspended sediment in the range 1.2 to 0.2 µm from Bothlin Burn. The concentration trend is similar where all the concentrations increased in autumn 2009 and winter 2010 and decreased in summer 2009 and 2010. The results indicate metal concentrations increasing in July with a low flow rate (0.325 m^3/s), in November 2009 with high flow rate (1.15 m^3/s) and February 2010 with low flow rate (0.393 m^3/s). Concentrations for Ca and Fe are slightly increased in May 2010, while K, Mn and Zn were increased in June 2010. The Mn

and Zn concentrations show similar seasonal trends. There are some correlations between metals, such as between Ca, Fe and Mg, (see table 5-17). Positive correlation was observed between Fe and Mg (P, < 0.05). A lower correlation was observed between Fe and Ca (P, < 0.01). A correlation also existed between Zn Ca and K (P, < 0.05).

Table 5-16 Correlations between concentrations of different metals in the 1.2 µm fraction from Bothlin Burn

	Fe	Zn	Mn	Ca	Mg
Zn	0.408				
	0.275				
Mn	0.702	0.065			
	0.035	0.868			
Ca	0.683	0.558	0.083		
	0.043	0.118	0.832		
Mg	0.036	0.496	-0.310	0.484	
	0.926	0.175	0.416	0.187	
K	0.782	0.524	0.254	0.799	0.303
	0.013	0.148	0.510	0.010	0.429

Cell Contents: Pearson correlation
P-Value

Table 5-17 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Bothlin Burn

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.471				
	0.201				
Mn_1	0.349	0.428			
	0.357	0.251			
Ca_1	0.788	0.691	0.570		
	0.012	0.039	0.109		
Mg_1	0.854	0.543	0.676	0.733	
	0.003	0.131	0.046	0.025	
K_1	0.483	0.696	0.235	0.401	0.510
	0.188	0.037	0.543	0.284	0.161

Cell Contents: Pearson correlation
P-Value

The data show the metal concentrations in the sediment > 1.2 µm fraction increased in both summer 2009 and summer 2010. In addition, the concentration in the larger sediment > 1.2 µm is higher than the concentration in the 1.2 and 0.2 µm fraction. On the other hand, the concentrations in the range 1.2 and 0.2 µm are increased in both autumn 2009 and winter 2010. The highest metal concentrations in the two fractions were measured in different months.

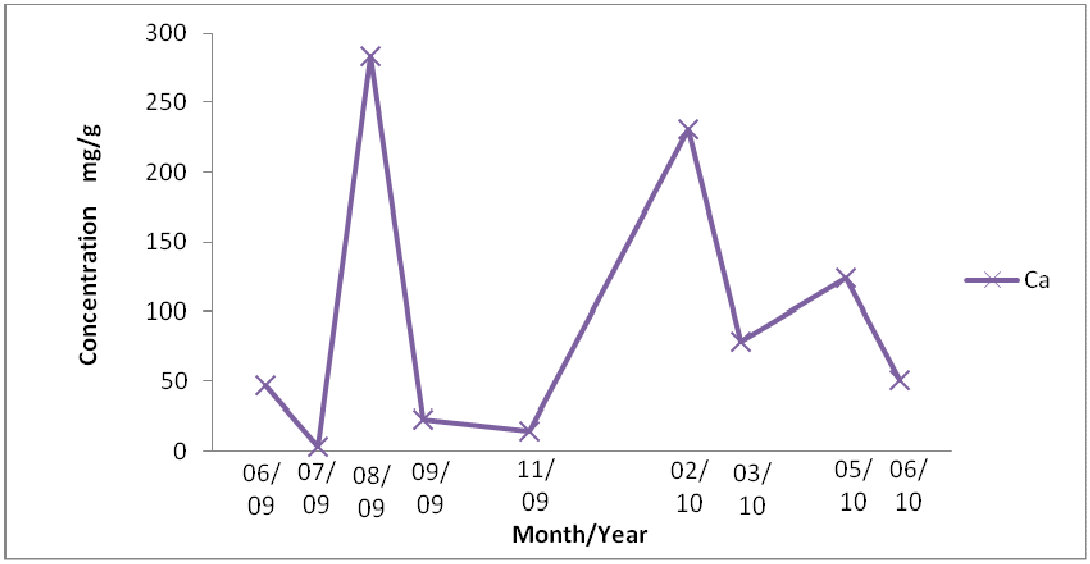

Figure 5- 38 Concentrations of Ca in suspended sediment (mg /g) of > 1.2 µm diameter from Bothlin Burn.

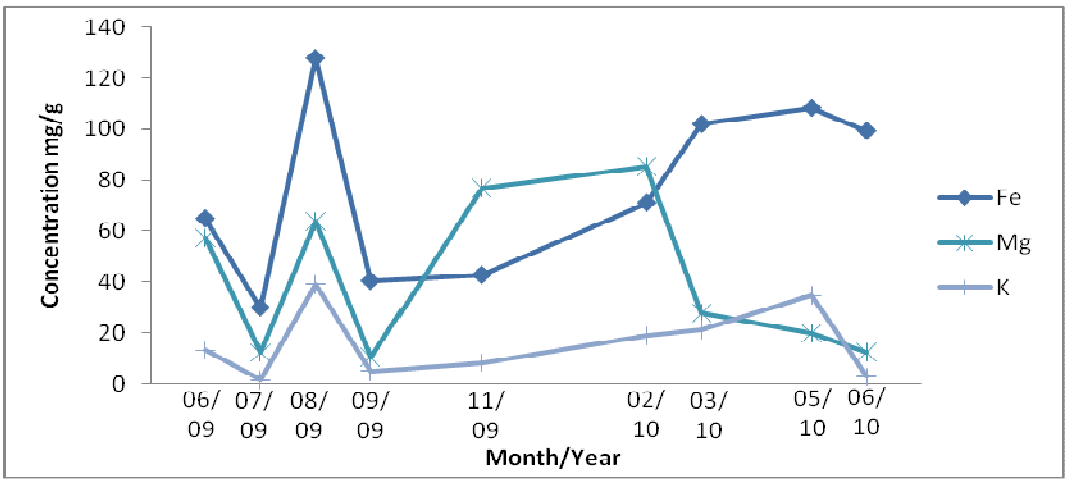

Figure 5- 39 Concentrations of Fe, K, and Mg in suspended sediment (mg /g) of > 1.2 µm diameter from Bothlin Burn.

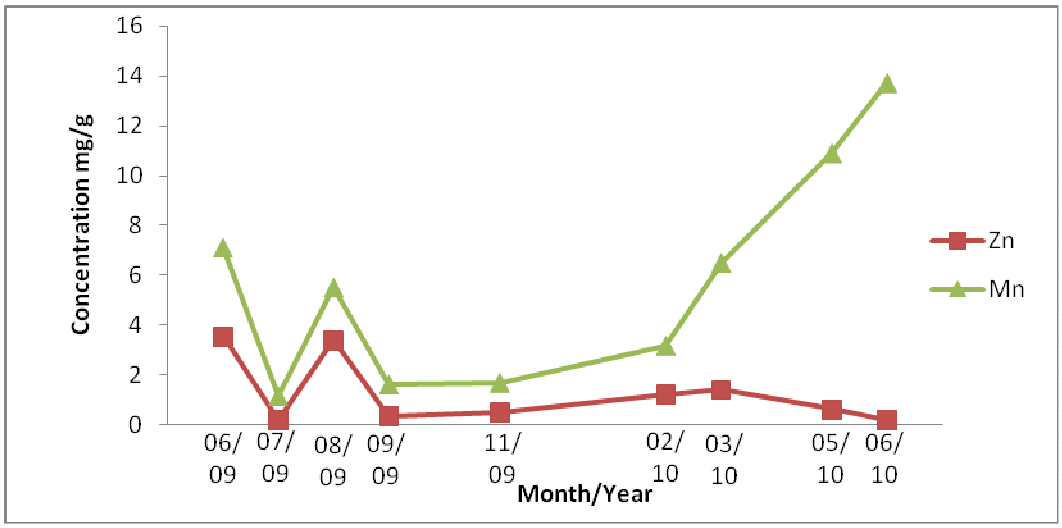

Figure 5- 40 Concentrations of Mn and Zn in suspended sediment (mg /g) of > 1.2 µm diameter from Bothlin Burn.

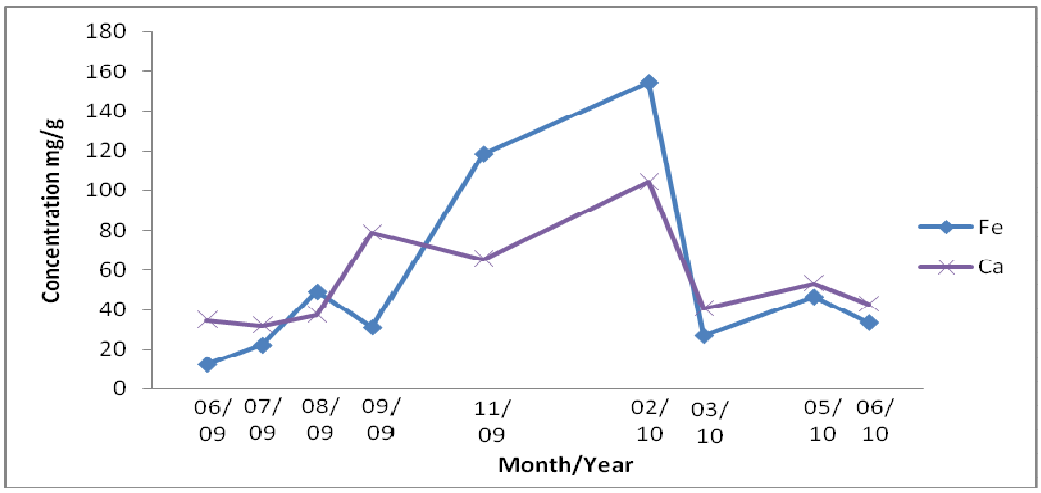

Figure 5- 41 Concentrations of Fe and Ca in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Bothlin Burn.

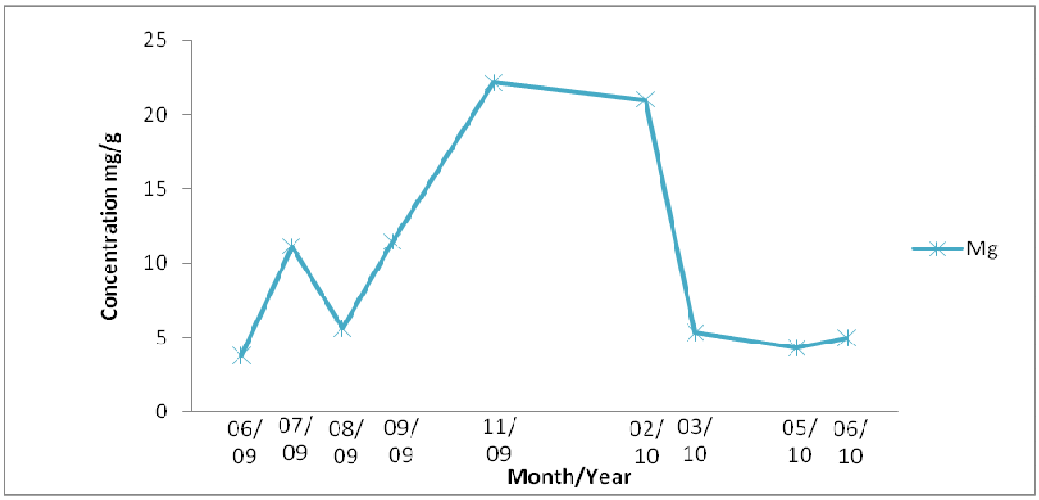

Figure 5- 42 Concentrations of Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Bothlin Burn.

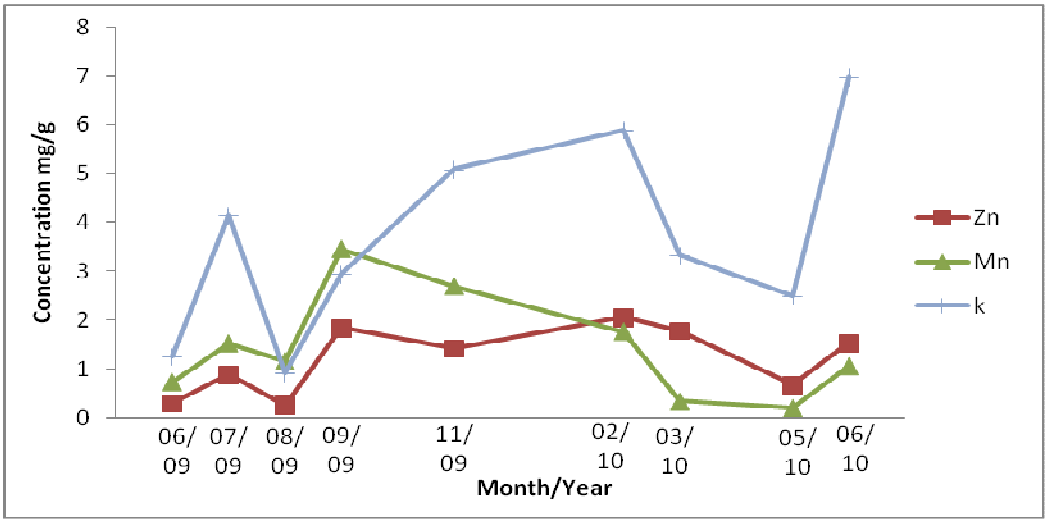

Figure 5- 43 Concentrations of K, Mn and Zn in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Bothlin Burn.

Figures 5-44 and 5-45 show the concentrations of metals in the suspended sediment in the > l.2 µm fraction from Luggie Burn. The concentration ranges of metals in the suspended sediment are shown in table 5-18. The concentrations are different throughout the nine sampling occasions. The results show that concentration of metals increased in June 2009 and in February 2010, and decreased in summer 2009 and 2010. Most concentrations were higher at the start of the sampling campaign in June 2009 with low flow rate (0.146 m^3/s). Also the concentrations for Ca, Fe and Mg were increased in February and March 2010 with a slight increase in the flow rate. The Mn concentration increased in May 2010 with low flow rate (0.238 m^3/s). The concentrations of metal in suspended sediment in the > 1.2 µm fraction from Bothlin Burn and Luggie Burn shows similar trends.

The results in table 5-19 show metals were positively correlated between some of metals. A positive correlation was observed between K and Fe, Ca and Zn (P, < 0.01), (P, < 0.02) and (P, < 0.01). In addition, a strong positive correlation was observed between (P, < 0.001) Zn, K, Mg and Mn. A correlation also existed between Ca and Fe and Zn (P, < 0.03) and (P, < 0.05).

Table 5-18 Ranges of metal concentrations (mg/g) in the > 1.2 µm and 1.2-0.2 µm diameter suspended sediment from Luggie Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	20–246	6.1–151	1.2-52.1	11-160	2.1–4.6	0.4–6.8
1.2 - 0.2 µm	26–220	8.6–231	1.4-21.1	4.8-72.1	0.5–6.3	0.2–6.3

The metal concentration ranges in the 1.2 - 0.2 µm fraction from Luggie Burn are shown in table 5-18 and seasonal trends in Figures 5-46, 5-47, and 5-48. The concentration trends are similar for the six metals. The concentrations increased in autumn 2009 and winter 2010. The concentration trends were similar for Fe, Mn and Zn. The concentrations of metals in February 2010 were the greatest with low flow rate (0.469 m^3/s). The concentrations of metals increased in winter 2010, and decreased in the summers of 2009 and 2010. The results in table 5-20 show metals were highly and positively correlated between the majorities of metals. A strong positive correlation was observed between Fe and other metals except Ca (P, < 0.001). In addition, a strong positive correlation was observed between (P, < 0.001) Zn, K, Mg and Mn. A correlation also existed between Mn, Ca, K, and Mg (P, < 0.005). A lower correlation was observed between Ca, K and Mg (P, < 0.05).

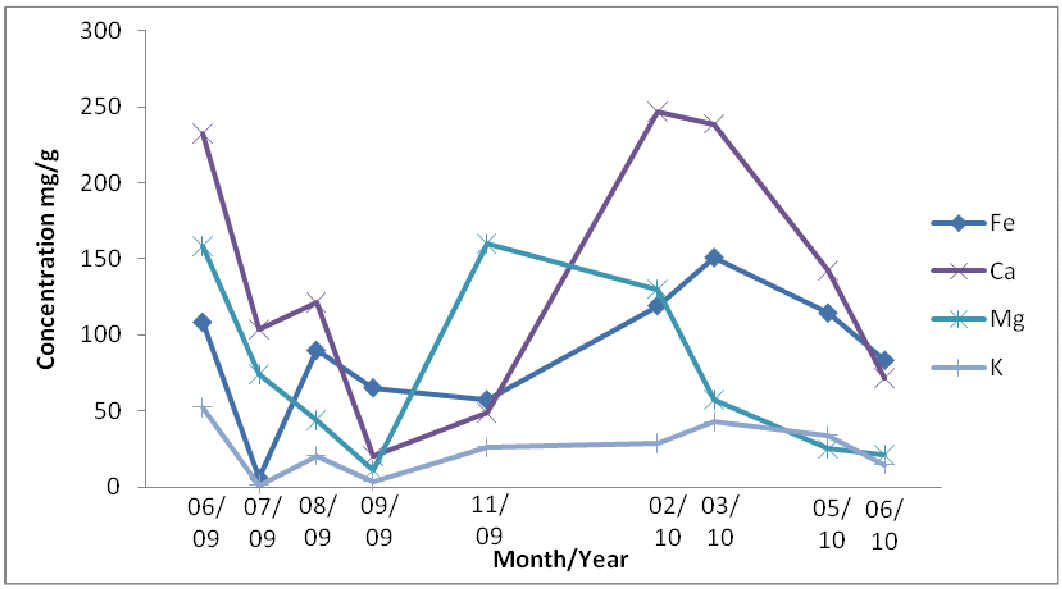

Figure 5- 44 Concentrations of Fe, Ca, K, and Mg in suspended sediment (mg/g) of > 1.2 µm diameter from Luggie Burn.

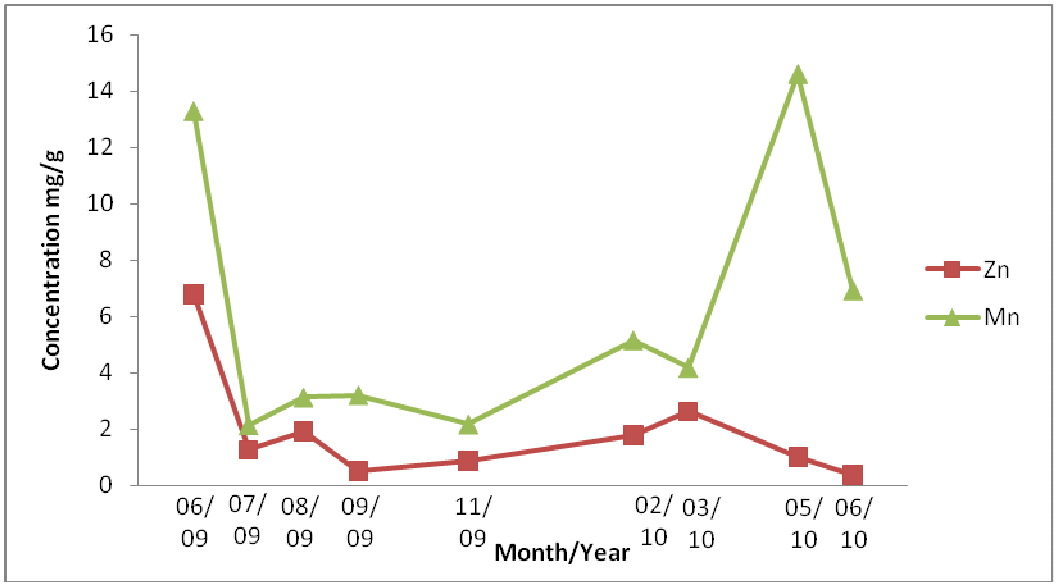

Figure 5- 45 Concentrations of Mn, and Zn in suspended sediment (mg/g) of > 1.2 µm diameter from Luggie Burn.

Table 5-19 Correlations between concentrations of different metals in the 1.2 µm fraction from Luggie Burn

	Fe	Zn	Mn	Ca	Mg
Zn	0.355				
	0.349				
Mn	0.455	0.480			
	0.218	0.191			
Ca	0.702	0.663	0.384		
	0.035	0.051	0.307		
Mg	0.004	0.561	0.027	0.393	
	0.991	0.116	0.945	0.295	
K	0.779	0.738	0.614	0.757	0.484
	0.013	0.023	0.078	0.018	0.187

Cell Contents: Pearson correlation
P-Value

Table 5-20 Correlations between concentrations of different metals in the 1.2- 0.2 µm fraction from Luggie Burn

	Fe_1	Zn_1	Mn_1	Ca_1	Mg_1
Zn_1	0.935				
	0.000				
Mn_1	0.936	0.943			
	0.000	0.000			
Ca_1	0.605	0.705	0.837		
	0.084	0.034	0.005		
Mg_1	0.975	0.950	0.940	0.673	
	0.000	0.000	0.000	0.047	
K_1	0.914	0.986	0.948	0.743	0.937
	0.001	0.000	0.000	0.022	0.000

Cell Contents: Pearson correlation
P-Value

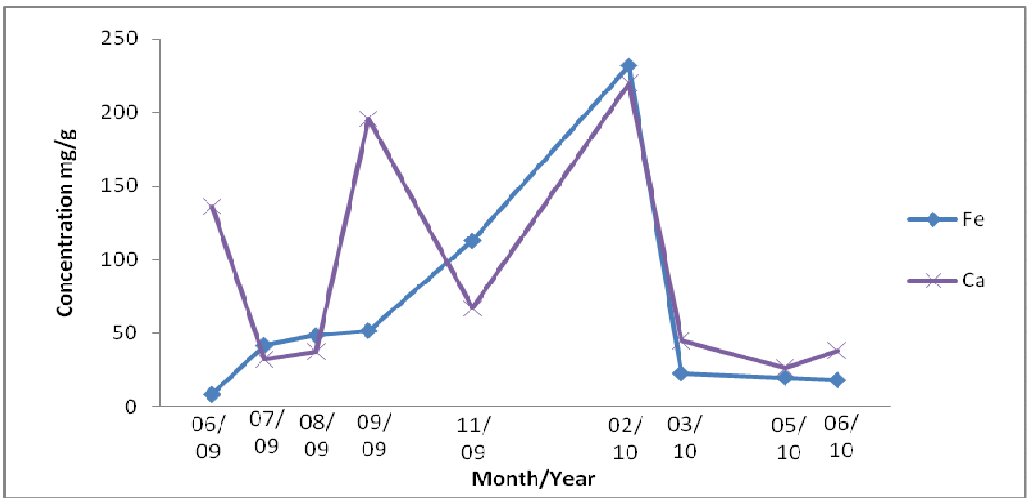

Figure 5- 46 Concentrations of Fe and Ca in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Luggie Burn.

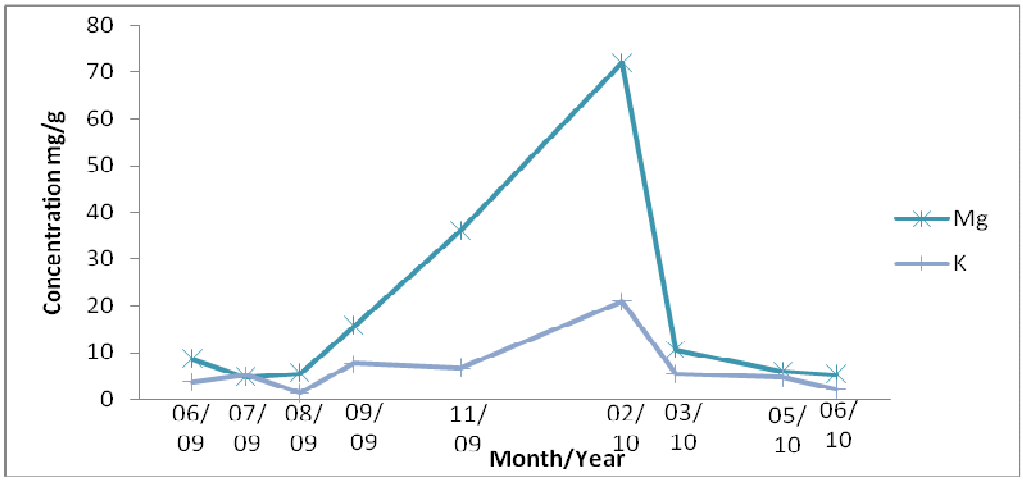

Figure 5- 47 Concentrations of K and Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Luggie Burn.

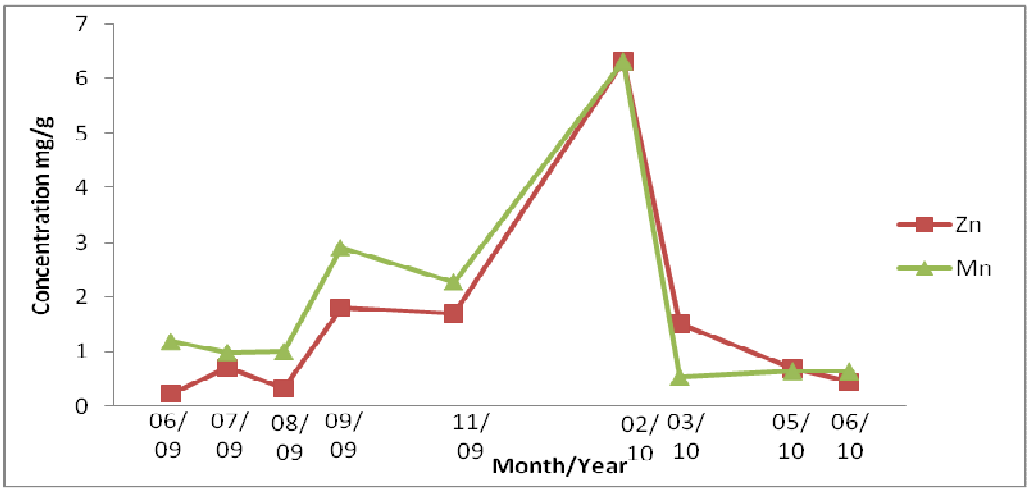

Figure 5- 48 Concentrations of Mn and Zn in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Luggie Burn.

Figures 5-49, 5-50, and 5-51 show the concentrations of metal in the suspended sediment in > 1.2 µm fraction from Cameron Burn. The concentration ranges for Ca, Fe, K, Mg, Mn and Zn in the suspended sediment are shown in table 5-21. The concentrations of the six metals show different trends. The figures show different concentration in the five sampling occasions. The highest metal concentrations are measured in August 2009, except for Mg which had maximum concentrations (126 mg/g) in July. On the other hand maximum concentration (8.9 mg/g) for Mn was measured in September 2009.

Table 5-21 Ranges of metal concentrations (mg/g) in the > 1.2 µm and 1.2 - 0.2 µm diameter suspended sediment from Cameron Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	41–299	61–121	29.1-84	44-152	4.8–8.9	0.7–4.5
1.2 - 0.2 µm	53–228	3.6–122	3.1-18.4	8-126	0.9–4.7	0.3–2.8

Figures 5-52, 5-53, and 5-54 show the concentrations of metals in the suspended sediment in the range 1.2 to 0.2 µm from Cameron Burn. The concentration ranges for Ca, Fe, K, Mg, Mn and Zn in the suspended sediment are shown in table 5-21. The trend is similar between most metals throughout the five sampling occasions, except for Ca. The highest metal concentrations were measured in November 2009, while for Ca the highest concentration (309 mg/g) was measured in June 2009.

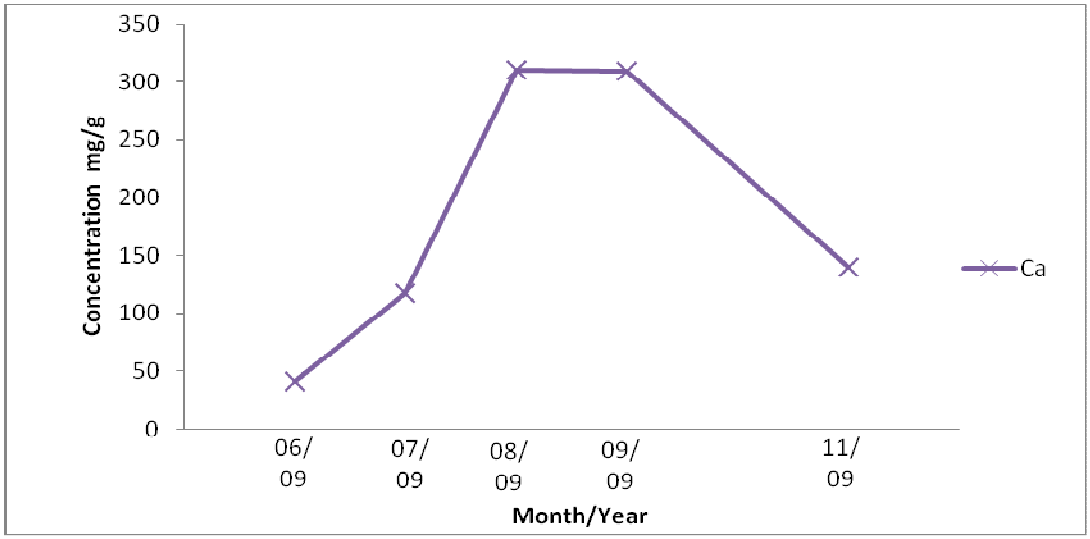

Figure 5- 49 Concentrations of Ca in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

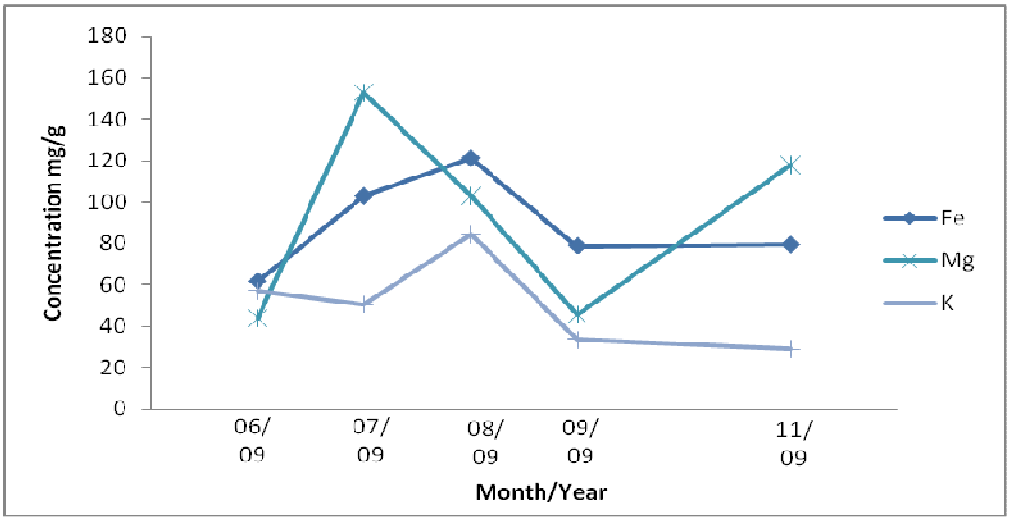

Figure 5- 50 Concentrations of Fe, K and Mg in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

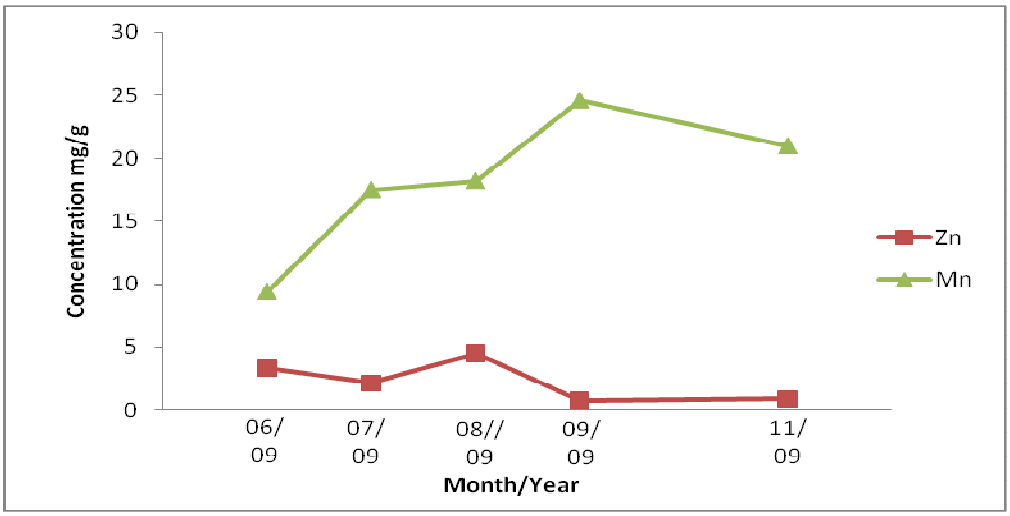

Figure 5- 51 Concentrations of Mn and Zn in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

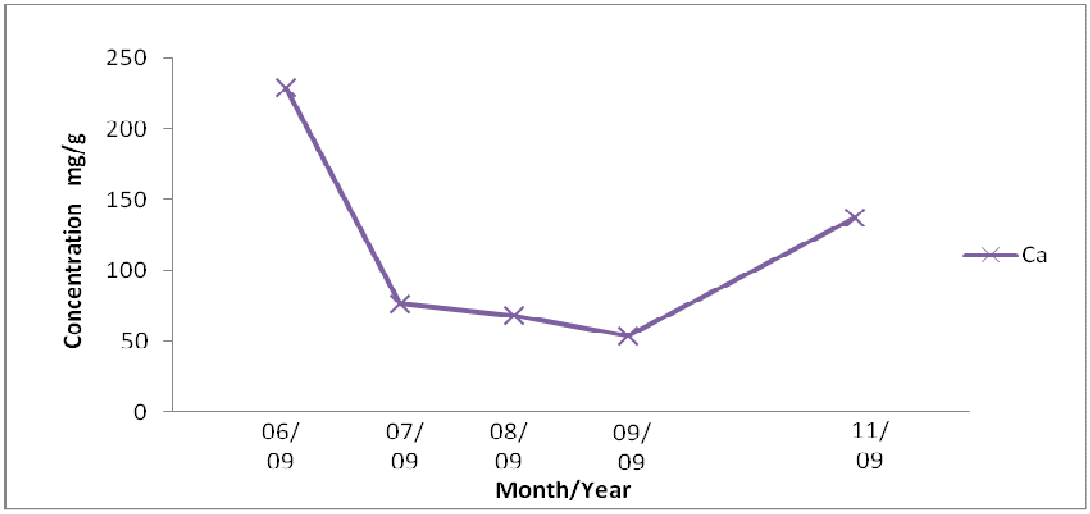

Figure 5- 52 Concentrations of Ca in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Cameron Burn.

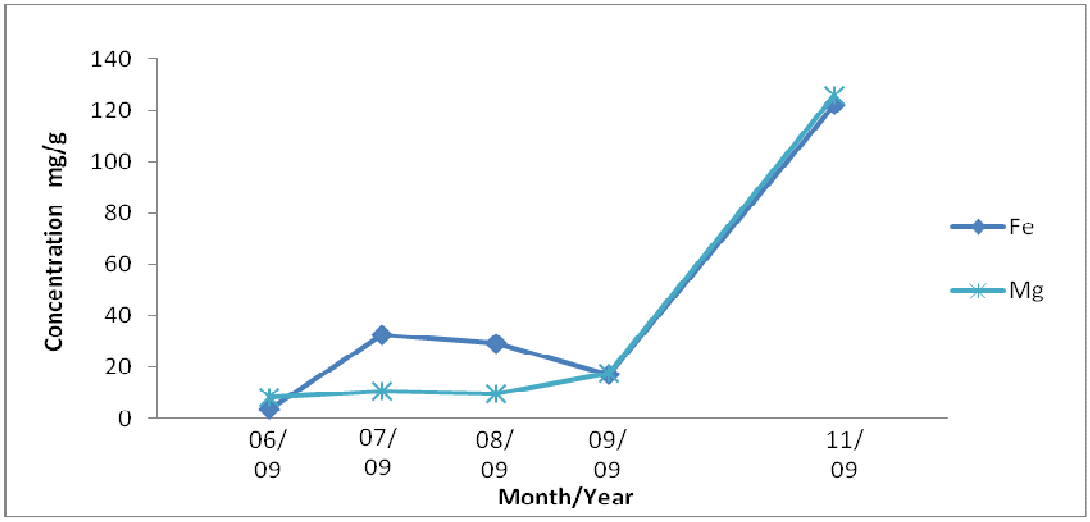

Figure 5- 53 Concentrations of Fe and Mg in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Cameron Burn.

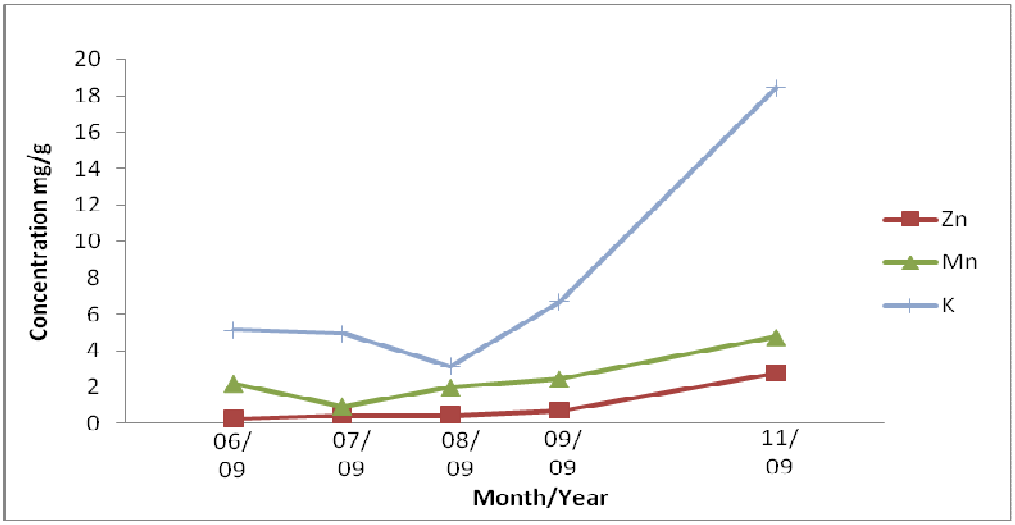

Figure 5- 54 Concentrations of K, Mn, and Zn in suspended sediment (mg/g) of (1.2- 0.2 µm) diameter from Cameron Burn.

The concentration ranges of metals in the > 1.2 µm fraction from Cameron Burn near to the landfill site are shown in table 5-22 and the seasonal trends in Figures 5-55, 5-56, and 5-57. The trend is different between the seven metals throughout the five occasions. The concentrations of Ca and Mg show similar trends. The concentrations for Ca and Mg were high in July 2009. In addition, the concentration trends are similar for Mn and Zn. Fe and K show similar trends with the highest metal concentrations measured in August and September 2009.

Table 5-22 Ranges of metal concentrations (mg/g) in the > 1.2 µm and 1.2-0.2 µm diameter suspended sediment from Cameron Burn

Sediment size	Ca	Fe	K	Mg	Mn	Zn
>1.2 µm	6–105.6	62–199	1.8-17.9	25-64.7	0.6–3.5	0.3–1.2
1.2 - 0.2 µm	5.9–23	0.7–19	2-12.6	2.9-11	0.3–1.6	0.1–0.3

Figures 5-58 and 5-59 show the concentrations in the range 1.2 and 0.2 µm near to the landfill inflow to Cameron Burn and the seasonal trends are shown in table 5-22. The concentrations measured between the seven metals of samples show different trends. The figures show the concentration trend is similar for Mn and Zn. On the other hand, the concentration trend for Fe, Ca and Mg shows the highest concentrations of the metals occur in different sampling months. The overall concentration trend is different for the different suspended particle ranges used. The metal concentrations associated with both size fractions (> 1.2 µm and 1.2 µm and 0.2 µm), increased in the summer. The contents for Fe, Zn, Mn, Ca, Mg, and K in the coarse (> 1.2 µm) suspended sediments are higher than those in finer sediments of 1.2- 0.2 µm.

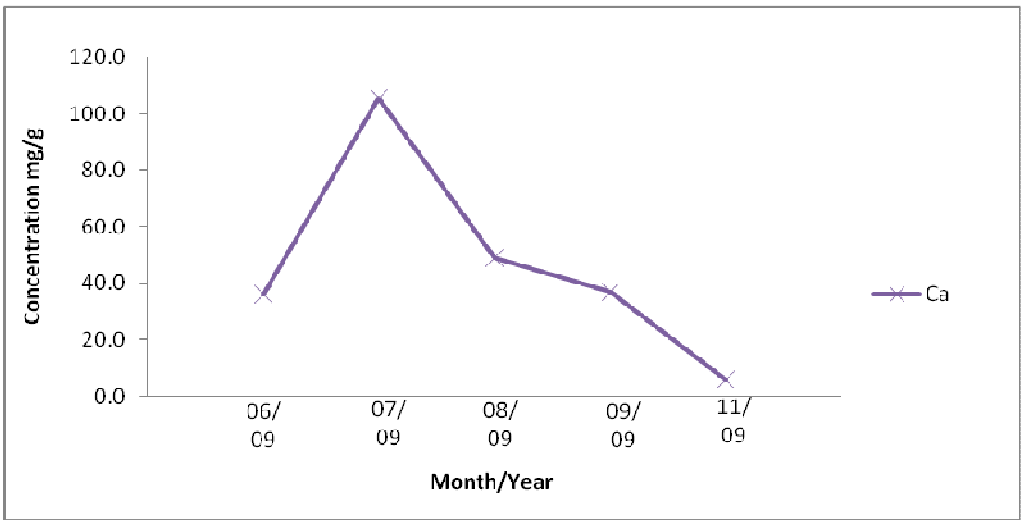

Figure 5- 55 Concentrations of Ca in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

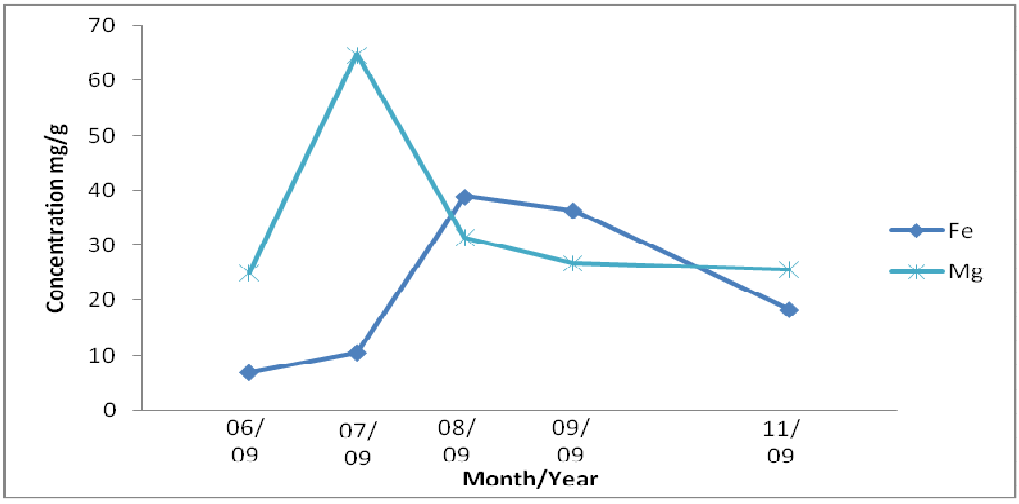

Figure 5- 56 Concentrations of Fe and Mg in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

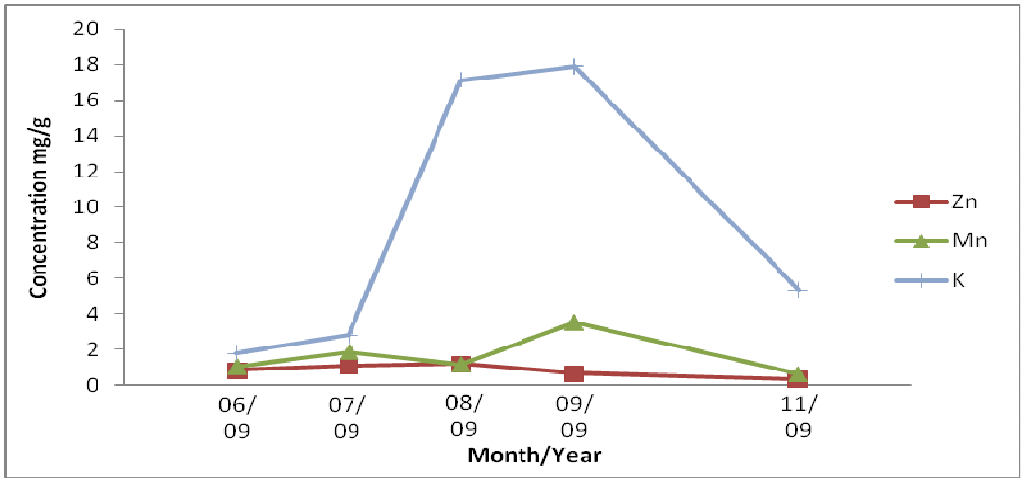

Figure 5- 57 Concentrations of K, Mn and Zn in suspended sediment (mg/g) of > 1.2 µm diameter from Cameron Burn.

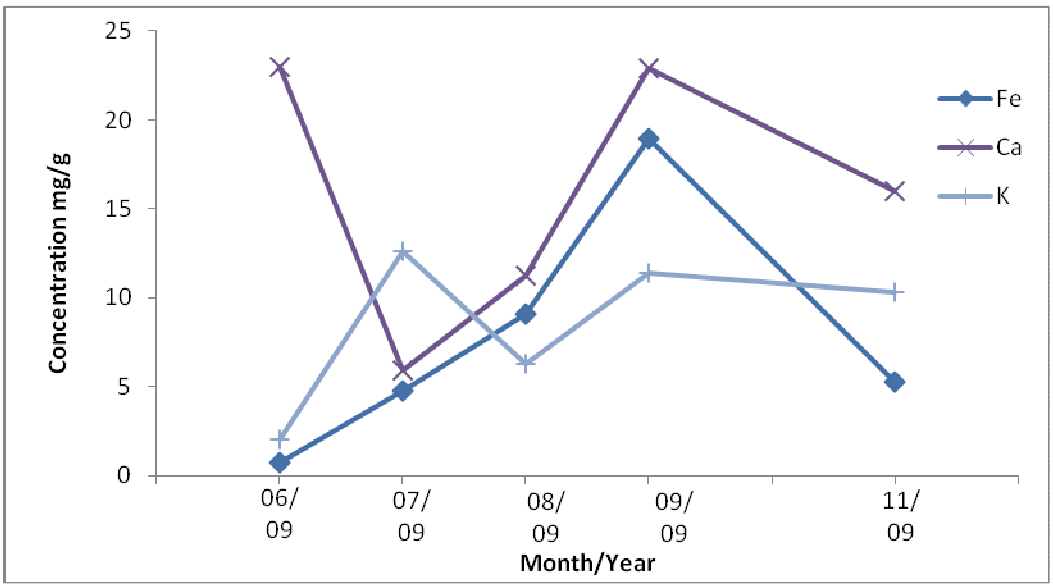

Figure 5- 58 Concentrations of Fe, Ca, and K in suspended sediment (mg/g) of (1.2-0.2 µm) diameter from Cameron Burn.

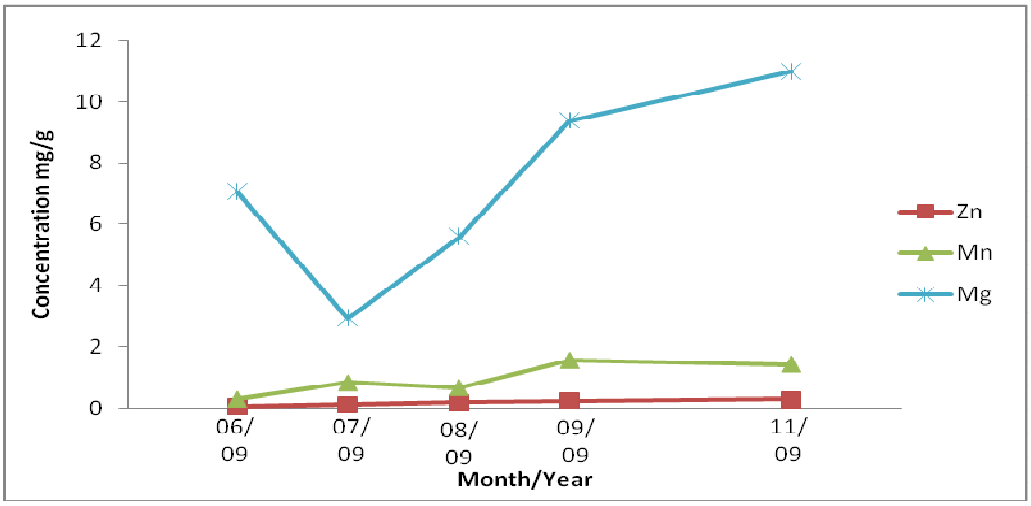

Figure 5- 59 Concentrations of Mn, Mg and Zn in suspended sediment (mg/g) of (1.2-0.2 µm) diameter from Cameron Burn.

5.2.1 Discussion

The results show increases in weight of sediment cause decreases in the concentrations of the six metals measured in the suspended sediment. That may be because of the coarse fraction sediment contains more minerals such as quartz and feldspar, which are low in Ferro magnesium minerals, whereas the fine fraction contains more of these Ca, Mg and Fe rich minerals (Irabien and Velasco 1999; Song et al. 1999). On the other hand, high concentrations of metal in the suspended sediment were measured with low mass of sediment. That may be because large metal concentration is associated with fine sized particles. The tributaries that showed similar trends in the mass of sediment, shows also similar trends of the metal concentrations in sediment.

The overall result shows there is no strong relationship between the flow rate and the concentrations of metal in the suspended sediment. Increased flow rate does not always cause an increase in the metal in the suspended sediment and decreased flow rate does not always cause a decrease in the metal in the suspended sediment. For example, the high flow rate in August 2009 resulted in increased metal in the suspended sediment in the > 1.2 µm diameter and a decrease of metal in the suspended sediment in the 1.2 to 0.2 µm fraction. On the other hand, the high flow rate in November 2009 caused a decrease in metal in the suspended sediment in the > 1.2 µm diameter and increase of metal in the suspended sediment in the 1.2 to 0.2 µm fraction. In addition, the metal in the suspended sediment in the > 1.2 µm diameter and in the 1.2 to 0.2 µm fraction were high with low flow rate such as in February and May 2010.

There are seasonal trends of the metal concentrations in the sediment, where the concentrations increase in the winter season or in the summer season. For example, metal concentrations increased in summer 2009 in the > 1.2 µm fraction with small sediment mass. On the other hand in some tributaries metal concentrations decreased with the high discharge in November 2009. Metal concentration in the sediment increased in winter 2010 in the > 1.2 µm fraction in the Allander Water, Bothlin Burn and Craigton Burn. In addition, metal concentrations in sediment decreased in autumn 2009 and increased in summer 2010 and winter 2010 in the Glazert Water and Craigmaddie Burn.

The concentration trends are similar for > 1.2 µm diameter sediment for Fe and Zn in the Bothlin Burn and Luggie Burn. In addition, the concentration trends are similar in the > 1.2 µm fraction for Zn in the Allander Water, Bothlin Burn, Craigtion Burn, and Luggie Burn. Metal concentrations in sediment were higher in autumn and summer 2009 in the range 1.2 to 0.2 µm. On the other hand, metal concentrations in sediment increased in winter 2010 in the 1.2 to 0.2 µm fraction in the Luggie, Craigton, Bothlin, Glazert, Craigmaddie and Allander Water. The concentration trends are similar in the range 1.2 to 0.2 µm for Fe in the Bothlin Burn and Glazert Water. In addition, the concentration trends are similar in the range 1.2 to 0.2 µm for Mg in the Allander, Craigmaddie and Bothlin. The metal concentrations in the 1.2 to 0.2 µm fraction increased in August and November 2009.

A general statistical analysis using Minitab Release 13.1 evaluated the correlations among the metals to indicate the similar behaviour of metals during transport in the river. The result shows two groups of metal correlations can be distinguished: the first one is for the particles in the >1.2 µm fraction; show little positive correlation with the other metals. The second group shows large a positive correlation between metals in the 1.2 - 0.2 µm fraction. These differences may be due to the different nature of the suspended sediment matter and metal in the two size fractions not controlled by a single geochemical component. The overall result shows correlations between Fe, Mn and Mg metals and the other metals in most of the tributaries. That may be because these metals were coated on the surface of the suspended sediment, because of the high level of secondary minerals. The secondary minerals for Fe, Mg and Mn show good correlations, most of the metals, compared with others that show only weak correlations. The elements weathered from the parent rocks may be bound as oxide phase.

From the results of the current study, there is no source of contamination in all sampling sites from the River Kelvin tributaries. That will indicate the metal concentrations in the suspended sediment may be due to erosion of soil, weathering of parent rocks and fertilizer from agricultural work. Levels of sedimentary Fe and Mn do not exceed those on average found in river system sediments that have been previously studied for World Rivers (Martin and Meybeck, 1979; Lesven et al., 2010; Hejabi et al., 2010). The metal concentration averages in the suspended sediment from the River Kelvin tributaries, for each sampling station are shown in Table 5-23, compared with data from other authors.

Metal levels in both fraction sizes are relatively similar in all sampling sites from River Kelvin tributaries. Metal concentrations in the particulate phase are quite similar in the current study as compared to those found by Hejabi et al. (2010). In the current study the

coarse particles are likely to transport metals more than fine particles in the Kelvin River tributaries, which is unusual. That may be due to an increase in the total metal transport in the stream.

Concentrations for Fe, Mn and Zn in the Kelvin river tributaries are similar to those in the Kabini River. Iron and Manganese and Zinc data in the >1.2 µm fraction are in good agreement with data from Hejabi et al. (2010), but lower than data from other authors such as Martin and Mebeck (1979), Van der Weijden et al. (1989), Quemerais et al. (1996), Yeats and Bewer (1982) and Sterckeman (2006). On the other hand, iron, magnesium and manganese concentrations in the range 1.2-0.2 µm fraction are in good agreement with data from Martin and Mebeck (1979), Van der Weijden et al. (1989), Quemerais et al. (1996), Yeats and Bewers (1982), and Sterckeman et al., (2006).

Table 5-23 Metal concentration (mg/g) in suspended sediment from River Kelvin tributaries compared with data from other authors

Tributaries River sediment fraction	Ca	Fe	K	Mg	Mn	Zn
Kelvin						
Craigton >1.2 µm	274	72.2	31.4	89	6.2	3.7
Allander >1.2 µm	202	84.7	36.2	143	5.7	3
Craigmaddie >1.2 µm	144	146	20.7	89	7.5	2
Glazert >1.2 µm	156	112	20.3	95.6	6.5	2.8
Bothlin >1.2 µm	106	76.3	16.2	40.7	5.7	1.3
Luggie >1.2 µm	136	88.5	24.7	75.8	6.1	1.9
Cameron B >1.2 µm	46.8	22	9	34.8	1.6	0.8
Average Kelvin	152.3	85.8	22.64	81.09	5.61	2.21
Craigton 1.2-0.2 µm	39	33	5.2	8.7	0.9	3
Allander 1.2-0.2 µm	53.7	50.4	9.9	13.8	3.2	3.2
Craigmaddie 1.2-0.2 µm	34.9	57.8	3.6	6.7	2	1.3
Glazert 1.2-0.2 µm	50.4	136	4.4	11.2	14.5	2.2
Bothlin 1.2-0.2 µm	54.4	54.8	3.7	10	1.4	1.2
Luggie 1.2-0.2 µm	88.6	61.9	6.5	18	1.8	1.5
Cameron B 1.2-0.2 µm	15	7.8	8.5	7	1	0.2
Average	48	57.4	5.97	10.8	3.5	1.8
Kabini						
Kattahalli 0.45 µm	-	194	-	-	7.02	3.07
Kattavadipura 0.45 µm	-	29.45	-	-	11.5	3.72
Kempasidd 0.45 µm	-	94.4	-	-	16.1	5.87
Nanjangud 0.45 µm	-	118	-	-	8.02	6.07
Mullura 0.45 µm	-	63.5	-	-	8.25	9.79
Thayur 0.45 µm	-	24.4	-	-	6.35	10.07
Biligerehundis 0.45 µm	-	186	-	-	6.02	1.57
Cauvery 0.45 µm	-	24.45	-	-	5.86	2.12
World river[b] 0.45 µm	21.5	48	20	6.46	1.05	0.35
Rhine[c]	-	32	-	-	1.70	-
St.Lawrenece[d]	-	25	-	-	-	-
St.Lawrenece[e]	-	53	-	-	1.69	-
St.Lawrenece[e] 0.45 µm	80	23	-	-	-	-
Deuler[f]	80.2	23.4		6.03	1.15	-

[a] Data from Hejabi et al., (2010)
[b]Data from Martin and Mebeck, (1979)
[c]Data from Van der Weijden et al., (1989)
[d] Data from Quemerais et al., (1996)
[e] Data from Yeats and Bewer, (1982)
[f]Data from Sterckeman et al., (2006)

5.2.2 Conclusion

The results of the seven tributaries survey provide an overview on the concentration for Ca, Fe, K, Mg, Mn and Zn in the suspended sediment along the entire course of the river Kelvin. The six metal species monitored in the tributaries of the Kelvin River showed distinct seasonal and spatial variability using periodic monthly grab sampling from 2009 and 2010. The suspended sediment mass at every tributary was different from one month to the next over the sampling months.

The overall result indicated that the metal concentrations are always higher in the larger particles > 1.2 µm than in fine particles 1.2 and 0.2 µm in diameter. The result shows increase masses of sediment cause decreases in the metal concentrations in the sediment. In contrast decreased mass of sediment causes increases in the metal concentrations in the suspended sediment.

The highest concentration of the Ca, K and Zn associated with > 1.2 µm diameter were measured in Craigton Burn. Highest concentrations of the Mg were measured in Allander water, while the highest concentrations of the Fe and Mn were measured in the Glazert water. On the other hand, the concentration of Ca and Mg measured in Luggie Burn were the greatest among the particle fraction 1.2 µm and 0.2 µm diameters. The concentrations for K and Zn measured in Allander were the highest among all sites. The highest concentrations for Fe and Mn were measured in the Glazert water.

5.3 River Water Samples – Sediment weight per unit volume of water

The metal concentrations in sediment expressed as weight per unit volume of water are presented as mg m^{-3}, as they represent the amount of metal associated with suspended sediment per unit volume of river water. That may be of more accurate than the metal concentrations in the suspended sediment, in mg/g in terms of transport of heavy metal in the river system.

Figures 5-60 to 5-62 show metal concentrations associated with sediment per unit volume of river water in the larger particles fraction (> 1.2 μm) from Craigton Burn. The trend of metal concentration in sediment per unit volume of water is higher in the summer and autumn of 2009 and summer of 2010. While it lowers in the winter of 2010, except for Fe concentrations, which are higher in summer seasons, 2009 and 2010 as well as in winter 2010. Increasing the mass of sediment in July 2009 caused increased metal concentrations in the suspended sediment per unit volume of river water for Ca, K, Mg, Mn and Zn, but decreased metal concentrations for Fe. Similarly in June 2010 increased concentrations of K and Mn were associated with the large sediment mass. On the other hand, November 2009 saw augmented metal concentrations for Fe, Ca, K and Mg with high metal concentrations in suspended sediment and a small amount of sediment mass, except for Mn and Zn.

Metal concentrations in sediment per unit volume of water in the range 1.2- 0.2 μm from Craigton Burn are shown in figures 5-63 to 5-65. Variation in the level of metals concentration was demonstrated. For example, it ranged between 19-49 mg m^{-3} for Fe and 18-48 mg m^{-3} for Ca. The metal concentrations in sediment per unit volume of water increased in summer 2009 and 2010 compared with winter 2010, except for Fe and Mg, where concentrations were higher in February 2010 than in May and June 2010. Increases in the metal concentrations were observed in June 2009 for Ca, Fe, Mg and Zn. The metal concentrations remained more or less the same in September, November 2009 and February 2010 for most of the metals measured. The overall graphs indicate a clear trend throughout the 9 occasions in both size fractions >1.2 μm and in the range 1.2 μm to 0.2 μm. High metal concentrations associated with suspended sediment per unit volume of river water were displayed in the summer of 2009 and the low metal concentration in the winter of 2010. Increased sediment mass did not increase the metal concentrations in sediment per unit volume of river water in the 1.2 to 0.2 μm fraction in August 2009 and June 2010. On the other hand, the metal concentration in the larger sediment (> 1.2 μm) was higher than the metal concentration associated with range 1.2 μm to 0.2 μm fractions.

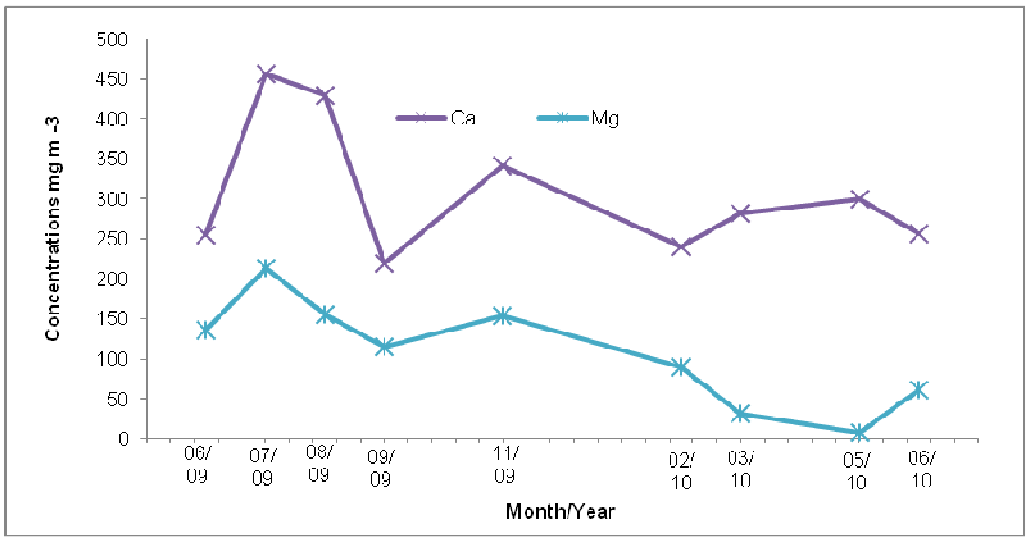

Figure 5- 60 Concentrations of Ca and Mg associated with suspended particles > 1.2 µm diameter in water from Craigton Burn (mg m^{-3}).

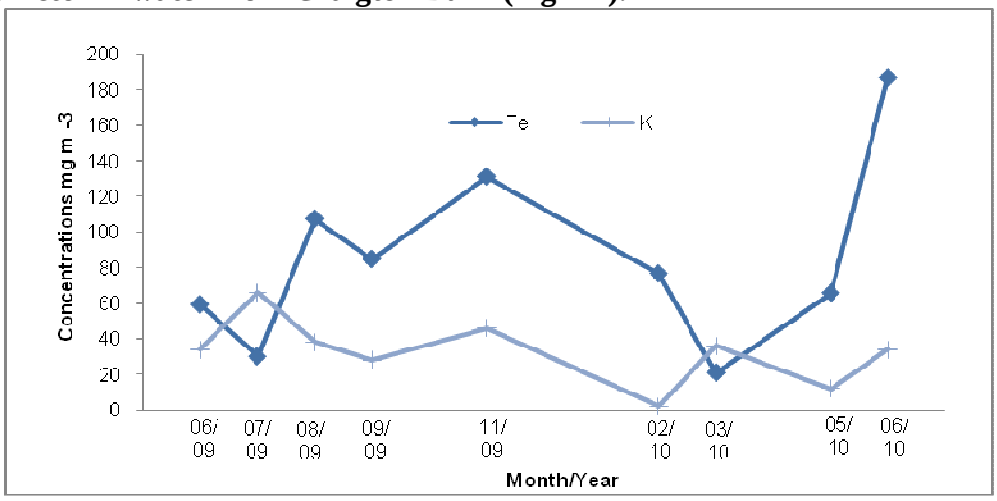

Figure 5- 61 Concentrations of Fe and K associated with suspended particles > 1.2 µm diameter in water from Craigton Burn (mg m^{-3}).

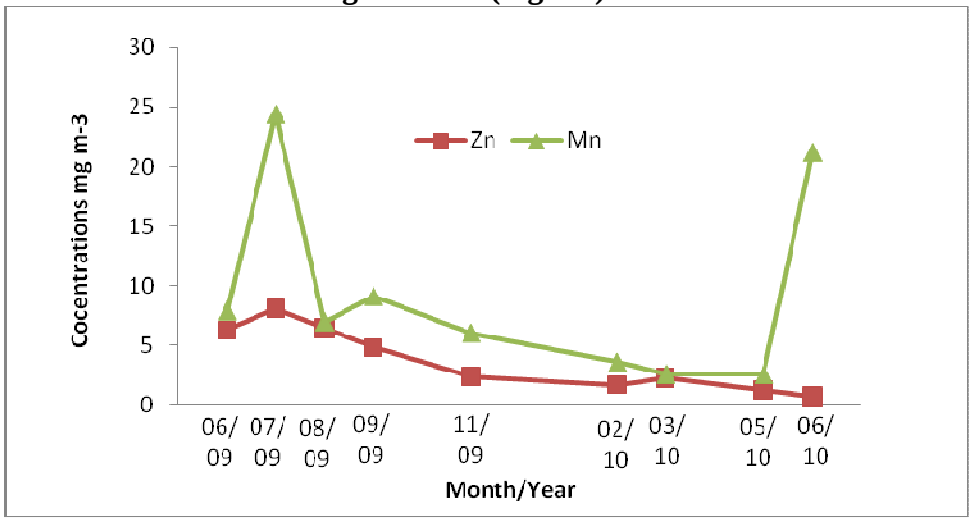

Figure 5- 62 Concentrations of Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Craigton Burn (mg m^{-3}).

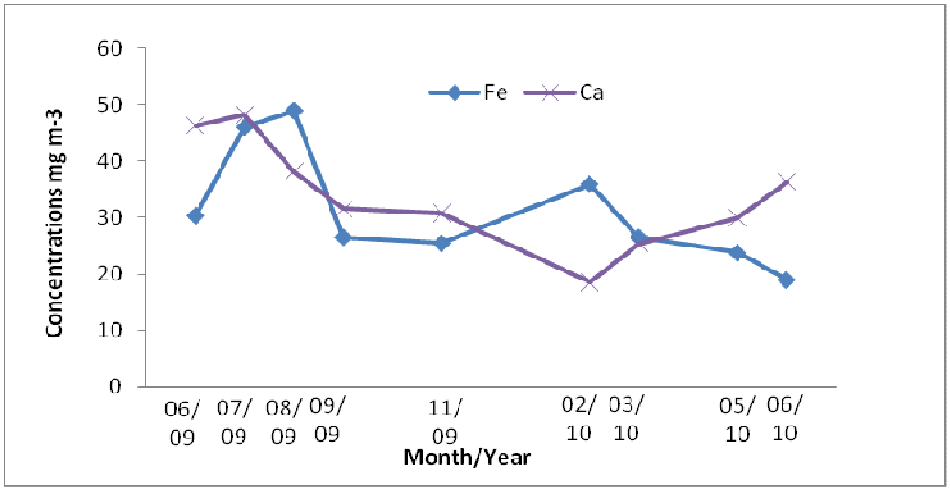

Figure 5- 63 Concentrations of Fe and Ca associated with suspended particles (1.2 - 0.2 µm) diameter in water from Craigton Burn (mg m^{-3}).

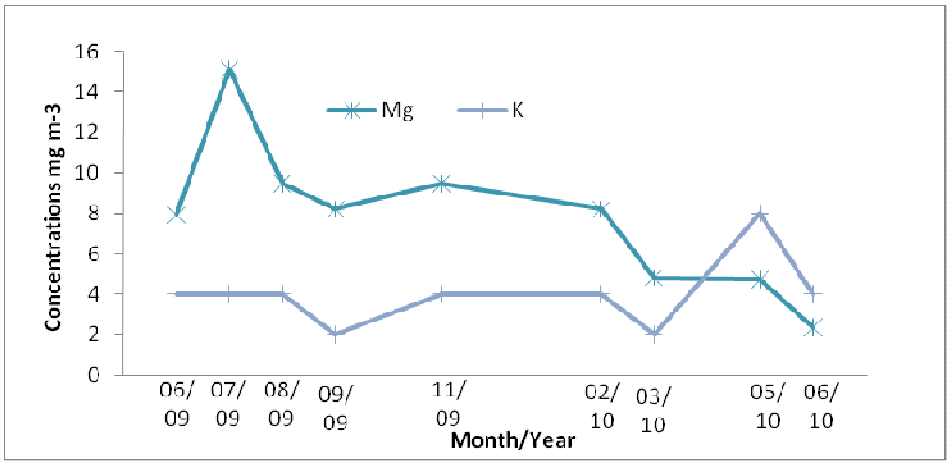

Figure 5- 64 Concentrations of K and Mg associated with suspended particles (1.2-0.2 µm) diameter in water from Craigton Burn (mg m^{-3}).

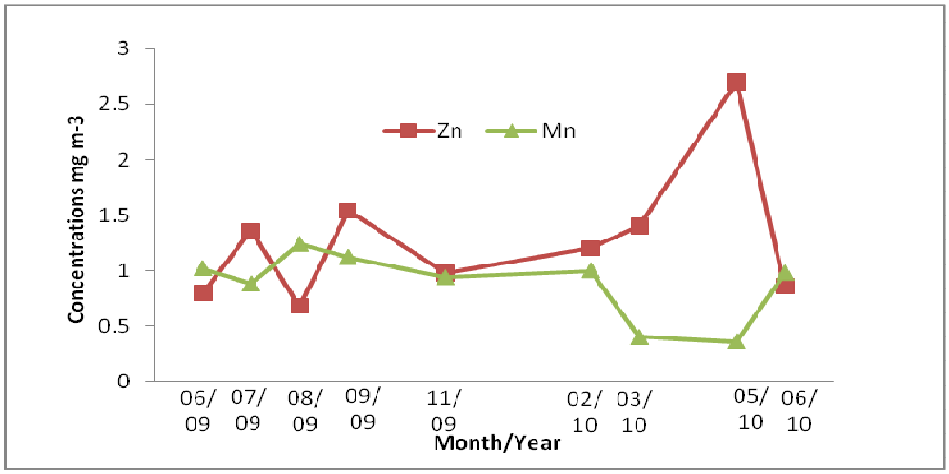

Figure 5- 65 Concentrations of Mn and Zn associated with suspended particles (1.2-0.2 µm) diameter in water from Craigton Burn (mg m^{-3}).

Figures 5-66 and 5-67 show a variety of metal concentrations in sediment per unit volume of water in the > 1.2 μm fraction from Allander water. The concentrations for Ca, K and Mg were higher in July 2009 and in February 2010 and lower in summer 2010. This could be due to increases in the mass of sediment with flow rate (0.390 m^3/s) in July 2009. While the concentrations for Ca and Fe were increasing in February 2010 with a decreased mass of sediment and high concentration in suspended sediment with gradually decreased flow rate on the sampling day, the Fe concentration was noticed to increase in July and August 2009 and to decrease in the winter and summer of 2010. The high metal concentration in August 2009 coincided with low mass of sediment in high flow rate (4.01 m^3/s). The metal concentrations for Mn and Zn were higher in the summer of 2009 (July) and lower in the winter and summer of 2010, except for Mn concentration which increased remarkably in June 2010. The highest metal concentrations in July 2009 were for Mg and Mn. In addition, the highest metal concentration for Ca (400 mg m^{-3}) was measured in February 2010 whereas the highest Zn concentration (8.18 mg m^{-3}) was measured in August 2009. The Fe and K show regular constant concentrations throughout the sampling months of winter 2010.

The metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fractions from Allander water are shown in Figures 5-68, 5-69 and 5-70. The metal concentrations were higher in the summer of 2009/2010 and lower in winter of 2010. The sediment mass in the range 1.2 to 0.2 μm was higher than that in the >1.2 μm fractions in August 2009. But metal concentrations in the range 1.2 to 0.2 μm were lower than the metal concentrations in the >1.2 μm fractions with high flow rate (4.01 m^3/s). That may be because of the effect of the high flow rate before the sampling day. The Mn and Zn concentrations show similar trends where concentration increases in summer 2009 (July) and summer 2010 (June) and decreases in the winter of 2010. Ca and Mg show regular concentrations throughout summer 2009 and decrease in the winter and summer of 2010. The highest concentration for Mn (6 mg m^{-3}) was measured in July 2009, whereas the greatest concentration of Fe (75.6 mg m^{-3}) was measured in August 2009. The K concentration was constant in summer 2009 and winter 2010, apart from increasing in November 2009 and June 2010.

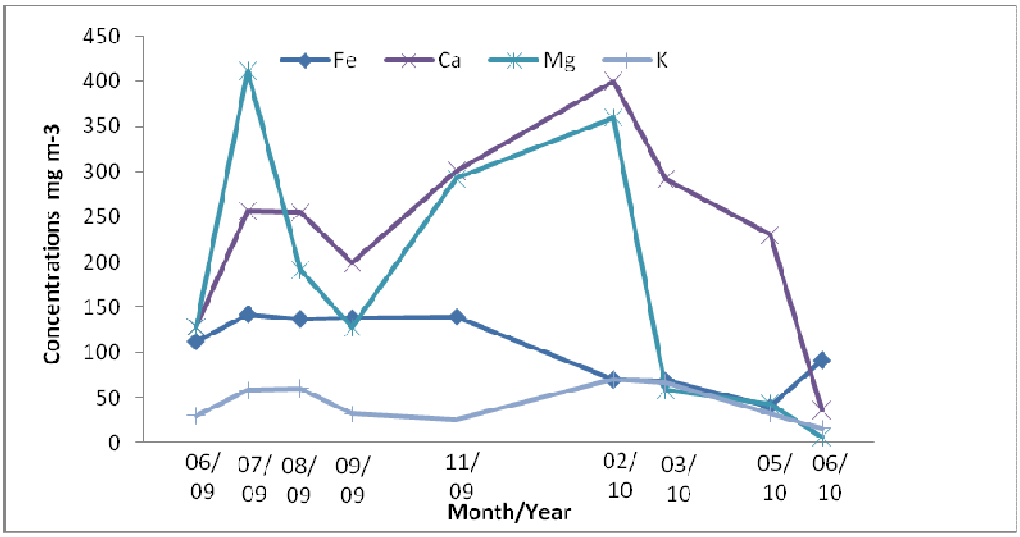

Figure 5- 66 Concentrations of Ca, Fe, K and Mg associated with suspended particles > 1.2 µm diameter in water from Allander Water (mg m^{-3}).

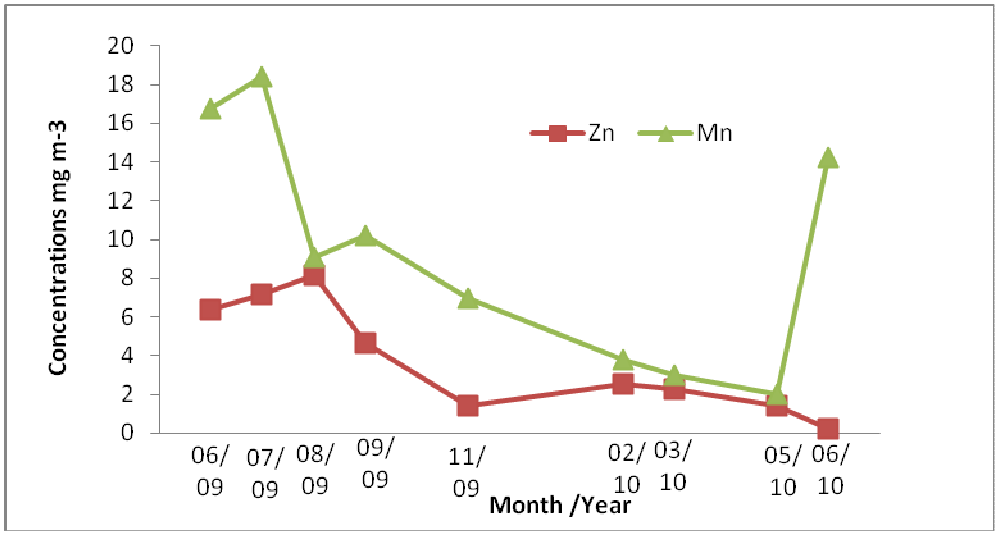

Figure 5- 67 Concentrations of Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Allander Water (mg m^{-3}).

The graphs indicate different trends throughout the 9 occasions in both size fractions > 1.2 µm and in the range 1.2 µm to 0.2 µm. The high metal concentration in sediment per unit volume of water in the >1.2 µm fraction was measured in winter. On the other hand, considerable metal concentrations were measured in the summer in sediment per unit volume of water in the 1.2 µm to 0.2 µm fraction range.

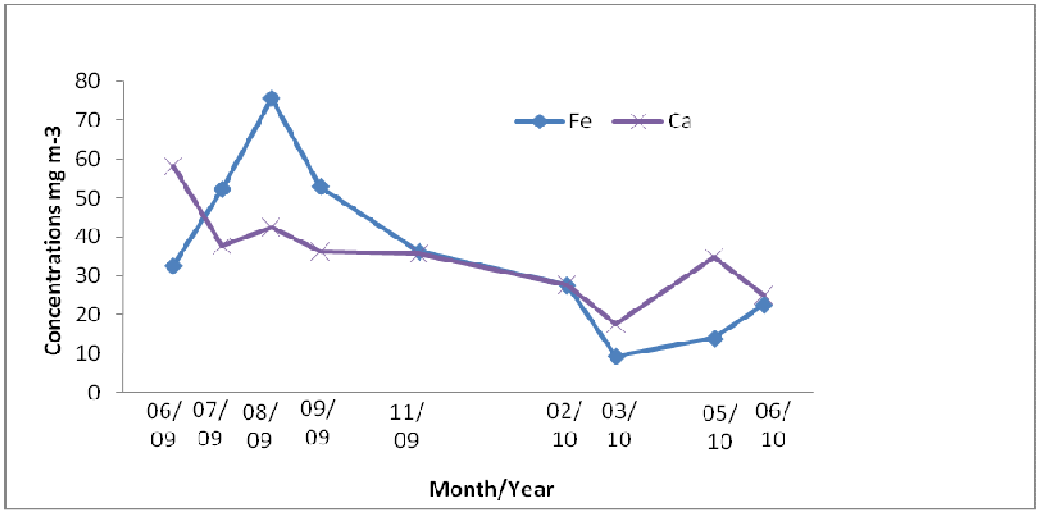

Figure 5- 68 Concentrations of Fe and Ca associated with suspended particles (1.2-0.2 µm) diameter in water from Allander Water (mg m^{-3}).

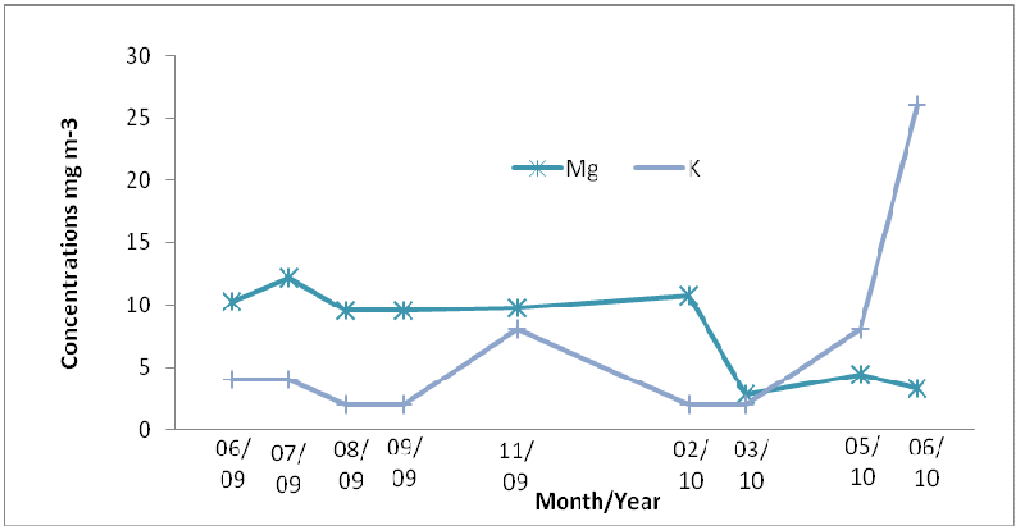

Figure 5- 69 Concentrations of K and Mg associated with suspended particles (1.2-0.2 µm) diameter in water from Allander Water (mg m^{-3}).

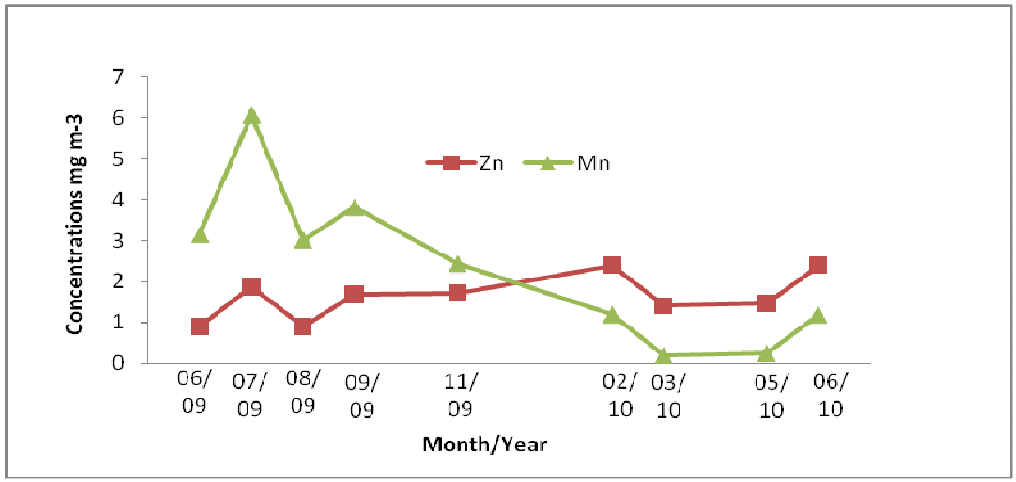

Figure 5- 70 Concentrations of Mn and Zn associated with suspended particles (1.2-0.2 µm) diameter in water from Allander Water (mg m^{-3}).

Figures 5-71 and 5-72 show the metal concentrations in sediment per unit volume of water in the > 1.2 μm fraction from Craigmaddie Burn. The figures demonstrate a range of concentrations for Fe between 96-421 mg m^{-3}, Ca 93-365 mg m^{-3} and Mg 30-288 mg m^{-3} respectively. The metal concentrations in sediment per unit volume of water for Ca, Fe, K, Mg and Mn were higher in the summer of 2009 (July and August). In addition, metal concentrations in sediment per unit volume of water was high in the summer of 2010 (June) with small sediment mass. The Zn concentration was higher in the summer of 2009 followed by dropping levels in the winter and summer of 2010. In November 2009 metal concentrations were higher with a major amount of mass of sediment, while metal concentration in suspended sediment was low, maybe due to dilution by the rainfall. The highest concentrations for Fe and Mn were measured in November 2009. The highest Mg (351 mg m^{-3}) concentration was measured in July 2009, while the highest metal concentrations for Ca and K were measured in March and June 2010.

The metal concentration in sediment per unit volume of water in the 1.2 μm to 0.2 μm from Craigmaddie Burn is shown in Figures 5-73, 5-74 and 5-75. The concentrations of metal in the weight of sediment per unit volume of water show similar trends. Most metal concentrations were higher in the summer of 2009 (July) and winter 2010 (February) and lower in summer 2010, with small mass of sediment. Moreover, the metal concentrations increased in February 2010, which may be attributed to increased metal discharge with snow melt. On the other hand, the sediment mass in the range 1.2 to 0.2 μm was higher than that in the > 1.2 μm fractions in August 2009, but low metal concentration was measured in the 1.2 to 0.2 μm fraction in August 2009. In July 2009 and February 2010 metal concentrations in sediment per unit volume of water increases with increased metal concentration in suspended sediment in the same months. The Ca, Fe, K, Mg and Zn concentrations increased in the winter and decreased in the summer of 2010. The Mn concentration was higher in summer 2009 and 2010 and decreased in the winter of 2010. Ca shows an irregular concentration throughout the summer of 2009 and winter 2010 and decreases in summer 2010.

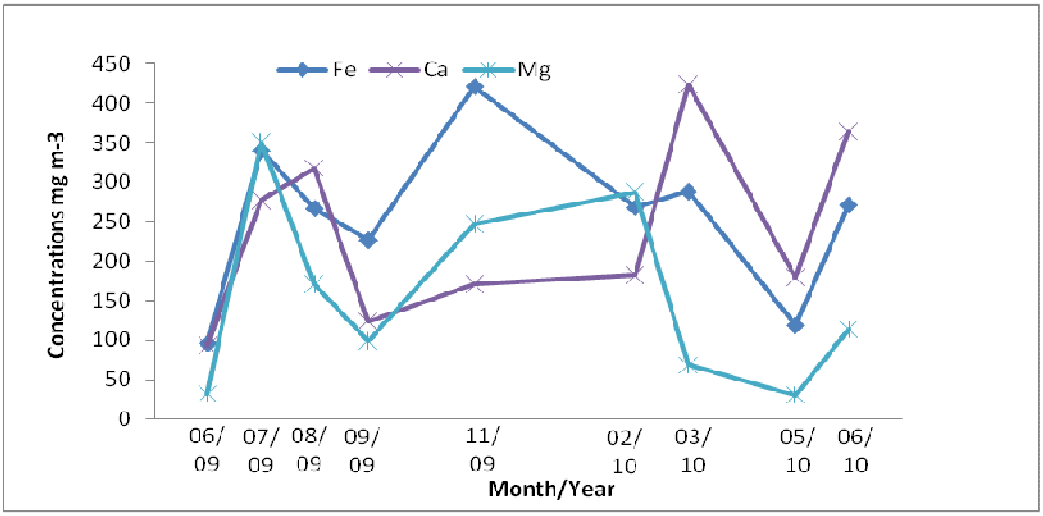

Figure 5- 71 Concentrations of Fe, Ca, and Mg associated with suspended particles > 1.2 µm diameter in water from Craigmaddie Burn (mg m^{-3}).

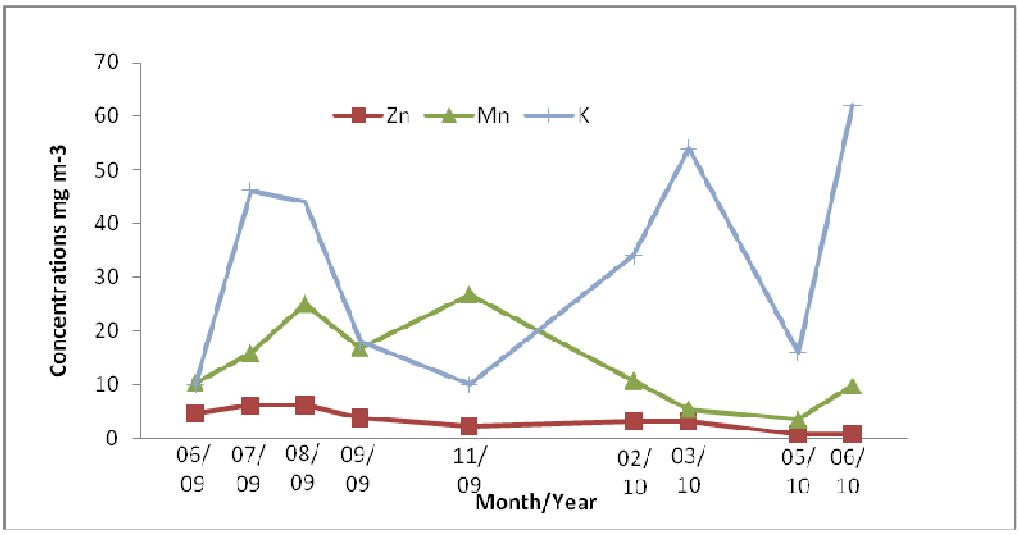

Figure 5- 72 Concentrations of K, Mn, and Zn associated with suspended particles > 1.2 µm diameter in water from Craigmaddie Burn (mg m^{-3}).

The data indicate a clear trend throughout the 9 occasions in both size fractions. High metal concentrations were measured in the summer of 2009 and low metal concentrations in winter of 2010. On the other hand, the metal concentration in the >1.2 µm fraction is higher than the metal concentration in the 1.2 µm - 0.2 µm fractions from Craigmaddie Burn.

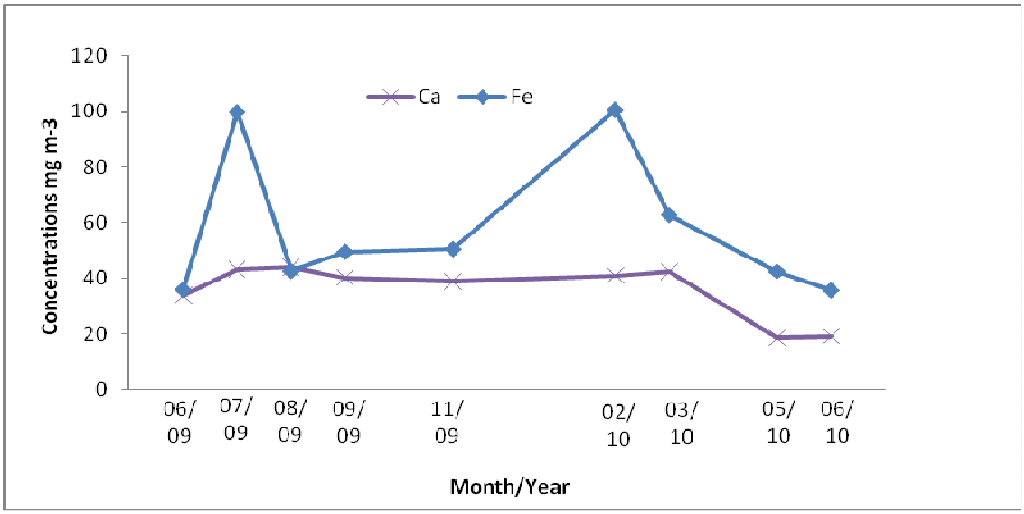

Figure 5- 73 Concentrations of Fe and Ca associated with suspended particles (1.2- 0.2 µm) diameter in water from Craigmaddie Burn (mg m^{-3}).

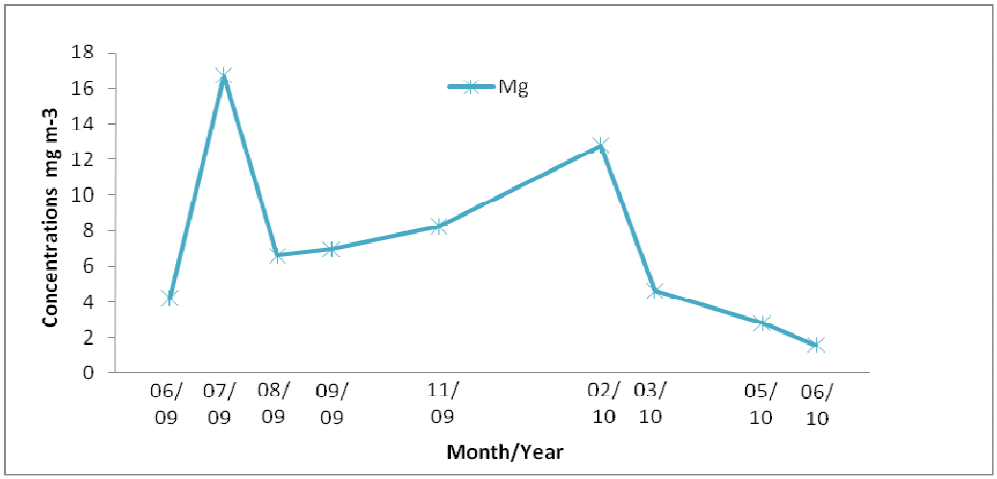

Figure 5- 74 Concentrations of Mg associated with suspended particles (1.2- 0.2 µm) diameter in water from Craigmaddie Burn (mg m^{-3}).

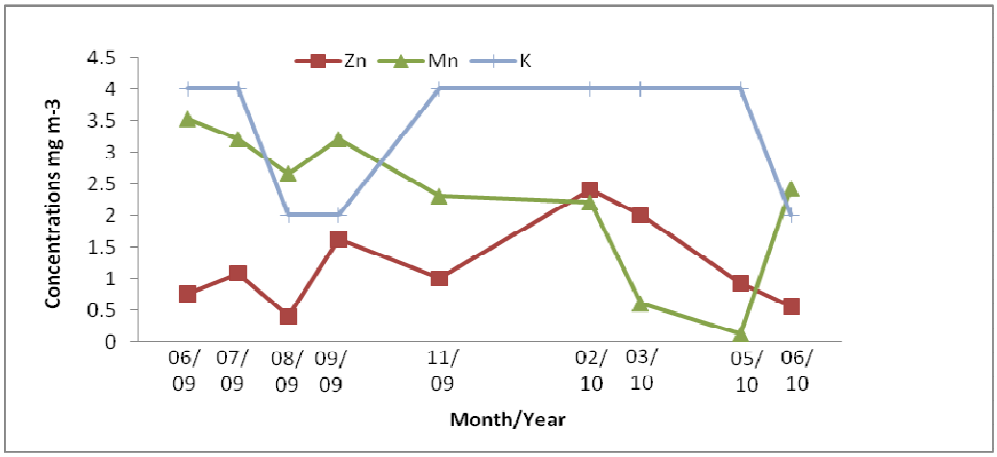

Figure 5- 75 Concentrations of K, Mn, and Zn associated with suspended particles (1.2- 0.2 µm) diameter in water from Craigmaddie Burn (mg m^{-3}).

Figures 5-76 and 5-77 show the range of metal concentrations in sediment per unit volume of water in the larger particle (>1.2 μm) fraction from Glazert water. The metal concentration trends are similar; the concentrations increase in July 2009 and in February and June 2010. The metal concentrations were higher in July 2009 with high flow rate (1.32 m^3/s). The metal concentrations were higher with low flow rate in February (0.562 m^3/s) and in June 2010 (0.274 m^3/s). All these concentrations were measured with a decreased amount of sediment mass. On the other hand, in November 2009 low metal concentrations were measured with increased sediment mass with high flow rate (4.32 m^3/s). In July 2009 February and June 2010 metal concentrations in sediment per unit volume of water increased with increases in the metal concentration in the same months. The highest concentrations for K and Mg were measured in July 2009. In addition, the greatest concentrations were measured in June 2010 for Ca (585 mg m^{-3}), and Fe (593 mg m^{-3}). The metal concentrations for Ca, Fe, K and Mg increased in February 2010. The concentration then reduced gradually in the following months.

The metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fractions from the Glazert water are shown in Figures 5-78, 5-79 and 5-80. The metal concentrations in sediment per unit volume of water are increased in the summer of 2010 compared with lower concentration in the summer of 2009 and winter of 2010. The concentrations for Ca, Fe and Zn were fairly constant in 2009 and 2010, except some increased Fe concentration in June 2010. The highest concentration of K is observed in March 2010. Mn concentration is higher in the summer of 2009 and 2010 and decreases in winter of 2010. In addition, the greatest concentration for Fe and Mn were measured in June 2010, with increasing sediment mass. The metal concentration is higher for the > 1.2 μm fraction than for the 1.2 μm to 0.2 μm fraction in the Glazert water. Metal concentrations in both of these fractions were higher in summer than in winter.

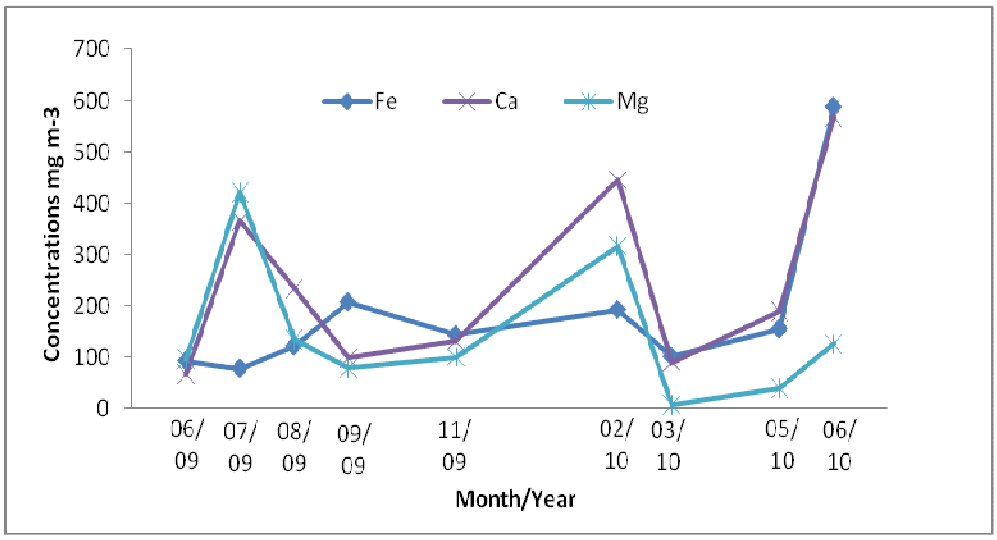

Figure 5- 76 Concentrations of Ca, Fe, and Mg associated with suspended particles > 1.2 µm diameter in water from Glazert water (mg m^{-3}).

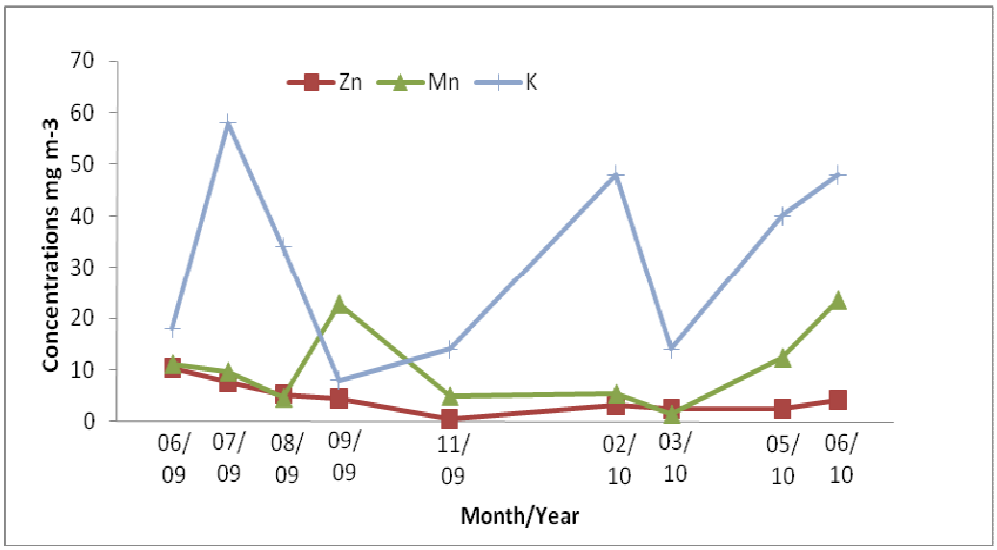

Figure 5- 77 Concentrations of K, Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Glazert water (mg m^{-3}).

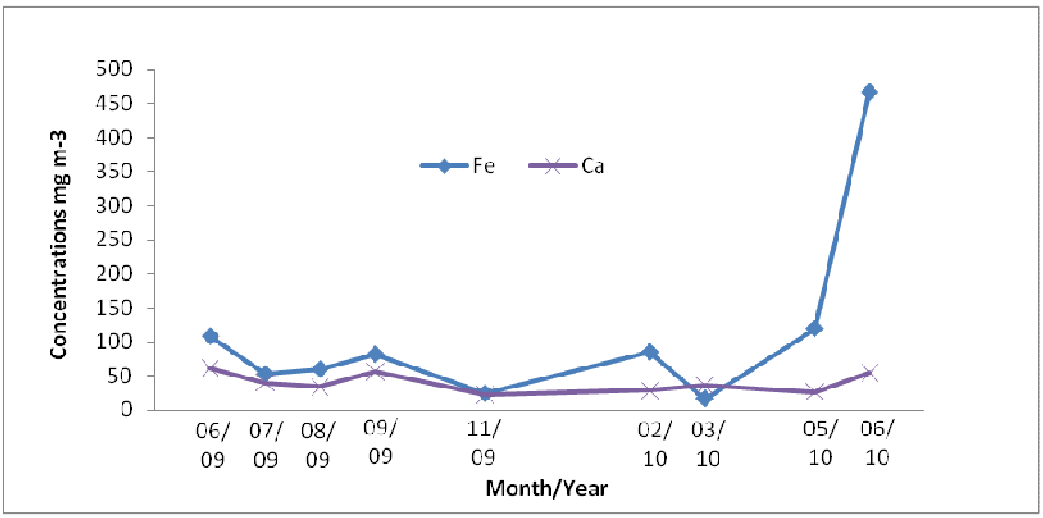

Figure 5- 78 Concentrations of Ca and Fe associated with suspended particles (1.2-0.2 µm) diameter in water from Glazert water (mg m^{-3}).

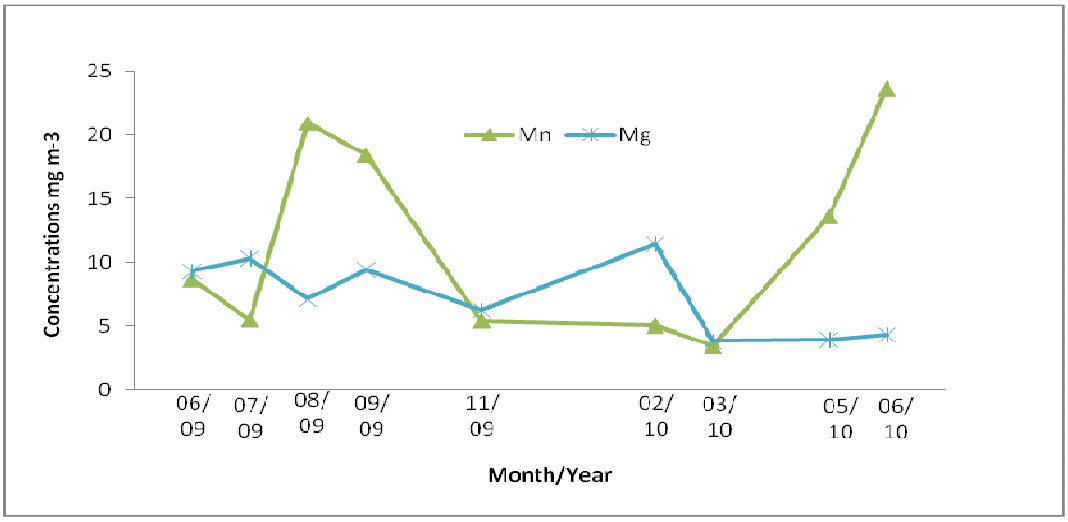

Figure 5- 79 Concentrations of Mg and Mn associated with suspended particles (1.2-0.2 µm) diameter in water from Glazert water (mg m^{-3}).

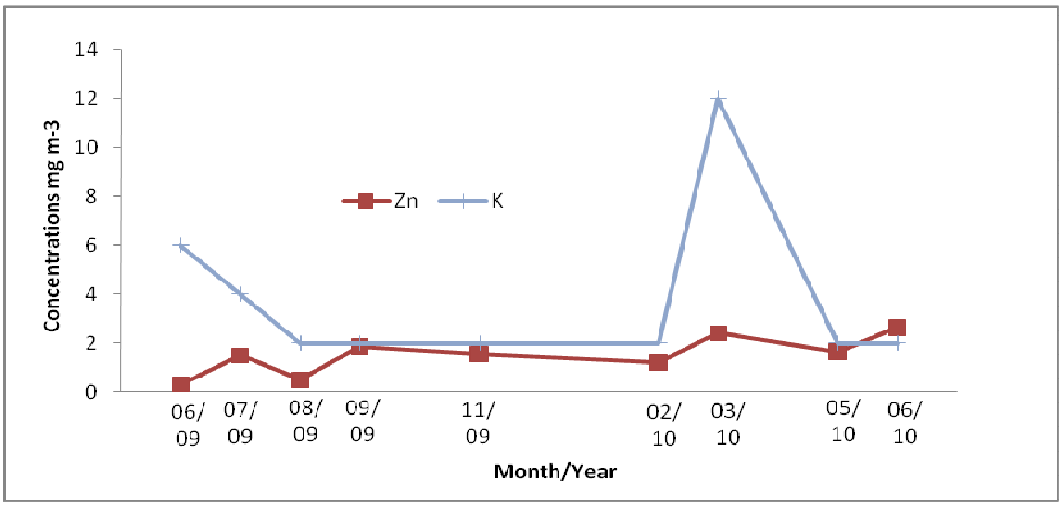

Figure 5- 80 Concentrations of K and Zn associated with suspended particles (1.2-0.2 µm) diameter in water from Glazert water (mg m^{-3}).

The metal concentrations in sediment per unit volume of water of Ca, Fe, K, Mg, Mn and Zn in the > 1.2 μm diameter fraction from Bothlin Burn are shown in figures 5-81, 5-82 and 5-83. All metal concentrations were higher in summer and autumn of 2009 and in winter of 2010. Metal concentration was higher in July 2009, with increased mass of sediment with low flow rate (0.325 m^3/s). Ca and K concentrations were higher in August 2009 with decreased mass of sediment in high flow rate (2.67 m^3/s) and with high concentration in suspended sediment. On the other hand, in November 2009 lower metal concentrations were measured, except for K and Mg with higher mass of sediment and high flow rate (1.15 m^3/s). The highest concentrations for Ca and K were measured in February 2010 and with high concentration in suspended sediment. Metal concentration was higher with small mass of sediment and low flow rate (0.469 m^3/s) in February 2010 leading to rising concentrations for Ca, Fe and Mg.

Figures 5-84, 5-85 and 5-86 show the variation in metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fraction from the Bothlin Burn. Metal concentrations were higher in the summer and autumn of 2009 and in winter of 2010 and decreased in the summer of 2010. The concentrations for K, Mg and Zn were higher in July 2009, whereas Ca, Fe and Mn concentrations were low with low flow rate (0.325 m^3/s). The highest metal concentrations measured in July 2009 were for K and Mg. In August 2009 the concentration increased for Ca, Fe and Mn with increasing sediment mass and high flow rate (2.67 m^3/s). Increases in metal concentrations in sediment per unit volume of water were observed in February 2010 for Ca, Fe, Mg, and Zn with increasing metal concentrations in the suspended sediment. The concentration of K, and Mn decreased in February 2010 and increased in June 2010.

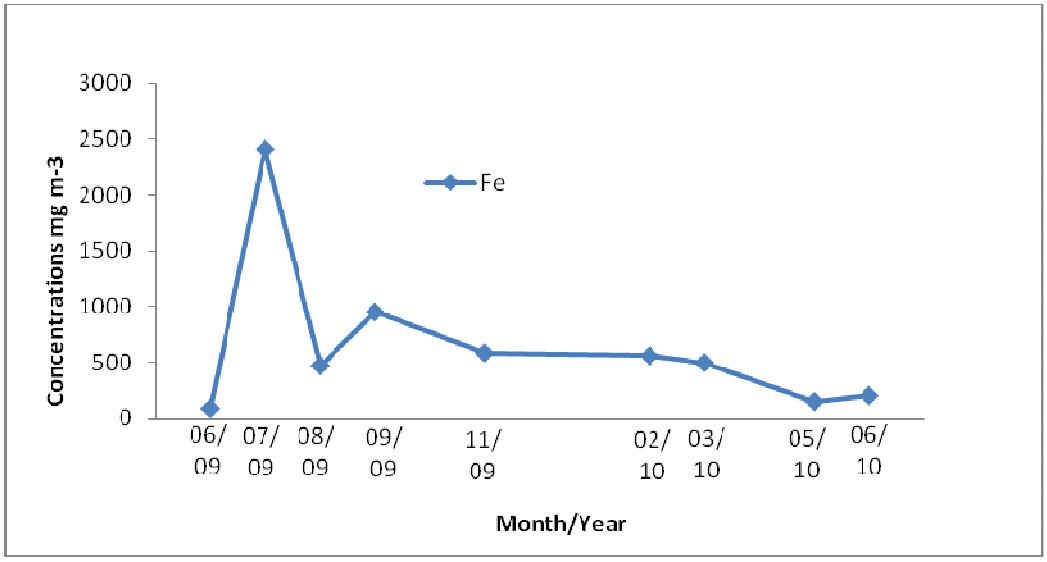

Figure 5- 81 Concentrations of Fe associated with suspended particles > 1.2 µm diameter in water from Bothlin Burn water (mg m^{-3}).

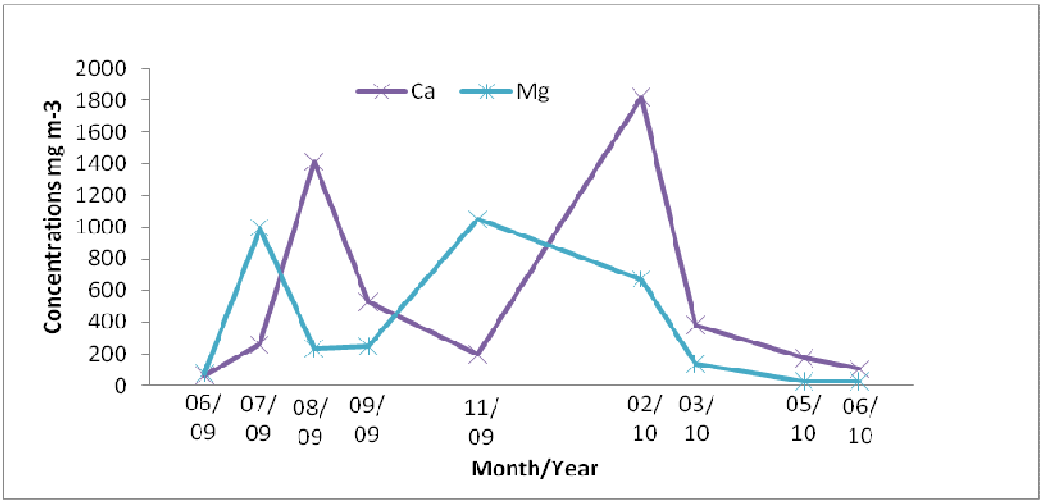

Figure 5- 82 Concentrations of Ca and Mg associated with suspended particles > 1.2 µm diameter in water from Bothlin Burn water (mg m^{-3}).

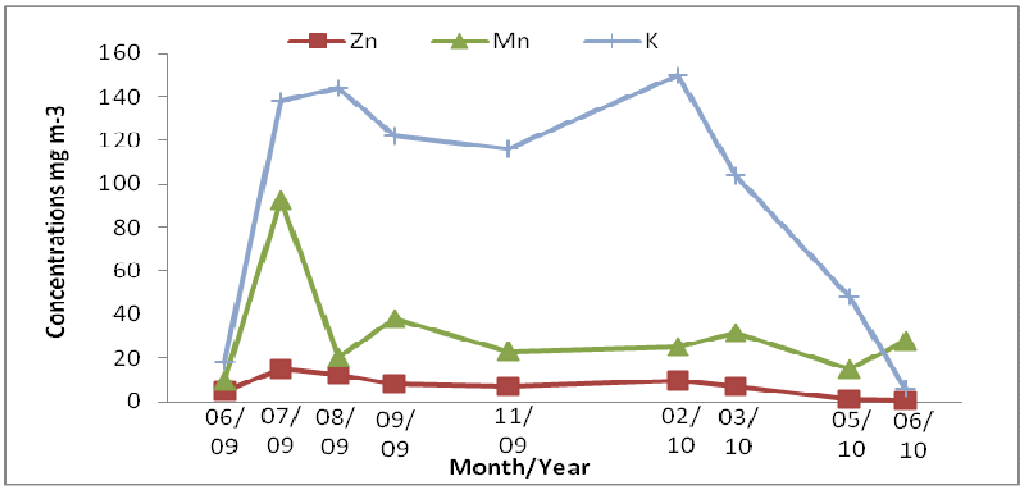

Figure 5- 83 Concentrations of K, Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Bothlin Burn water (mg m^{-3}).

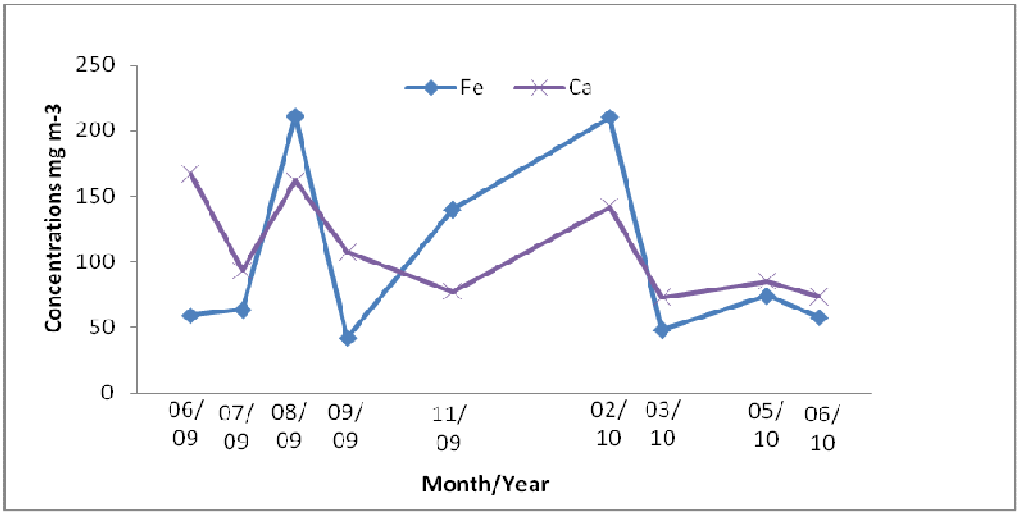

Figure 5- 84 Concentrations of Fe and Ca associated with suspended particles (1.2-0.2 µm) diameter in water from Bothlin Burn water (mg m^{-3}).

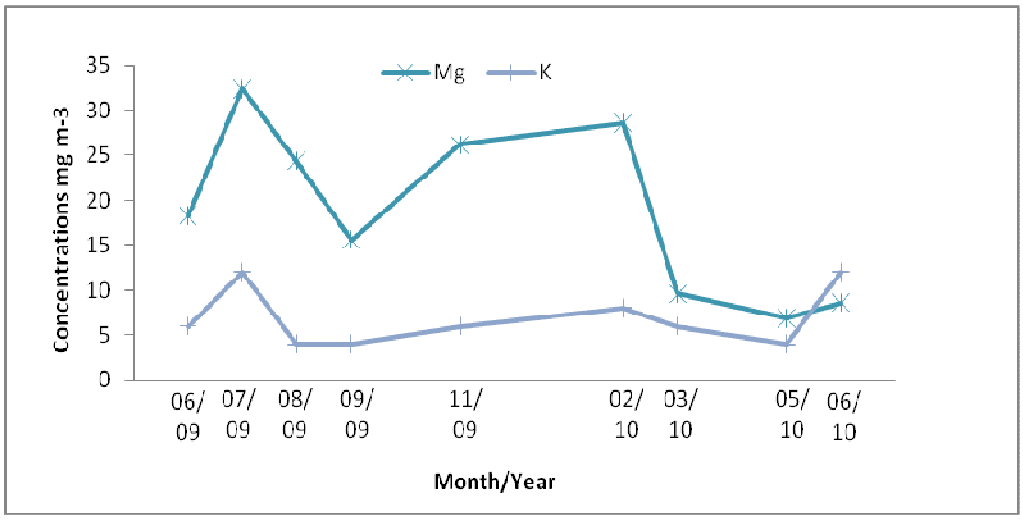

Figure 5- 85 Concentrations of K and Mg associated with suspended particles (1.2-0.2 µm) diameter in water from Bothlin Burn water (mg m^{-3}).

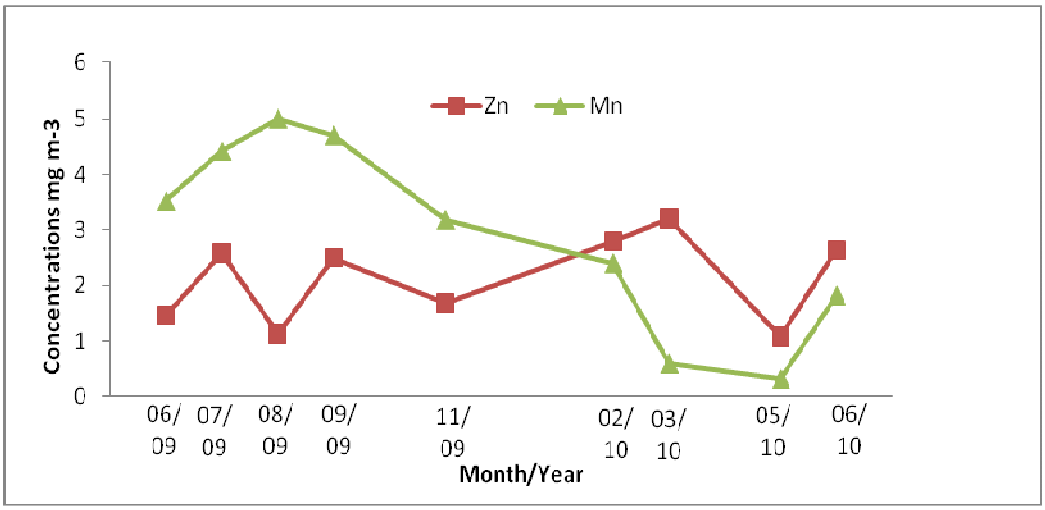

Figure 5- 86 Concentrations of Mn and Zn associated with suspended particles (1.2-0.2 µm) diameter in water from Bothlin Burn water (mg m^{-3}).

Metal concentrations for Luggie Burn in sediment per unit volume of water in the > 1.2 μm fraction are shown in figures 5-87, 88 and 5-89. Most of the metal concentrations in sediment per unit volume of water were higher in November 2009 with high flow rate (1.68 m^3/s) and lower in summer 2010. The concentrations for Mg, Mn and Zn were higher in July 2009 with increased sediment of mass in low flow rate (0.322 m^3/s). The concentrations for Ca, Fe and K were higher in August 2009 with decreased mass of sediment and high flow rate (3.86 m^3/s). Concentrations for Ca, Fe and Mg increased in November 2009 due perhaps to increased flow rate (1.68 m^3/s) and increase of mass of sediment. The concentration was high in February 2010 with low flow rate (0.469 m^3/s) for Fe, K, Mg and Mn. The figures show the concentration of the nine occasions of results to display an overall trend.

The metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fraction from Luggie Burn are shown in figures 5-90, 5-91 and 5-92. The concentrations for Ca, Fe, K, Mg, Mn and Zn were higher in the summer of 2009 and lower in the winter and summer of 2010. In November 2009 the metal concentrations in sediment per unit volume of water were high, that is likely caused by the high flow rate (1.68 m^3/s). While in July the metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fraction increase with low flow rate (0.332 m^3/s) and large mass of sediments. The K shows constant concentration through the winter and summer of 2010.

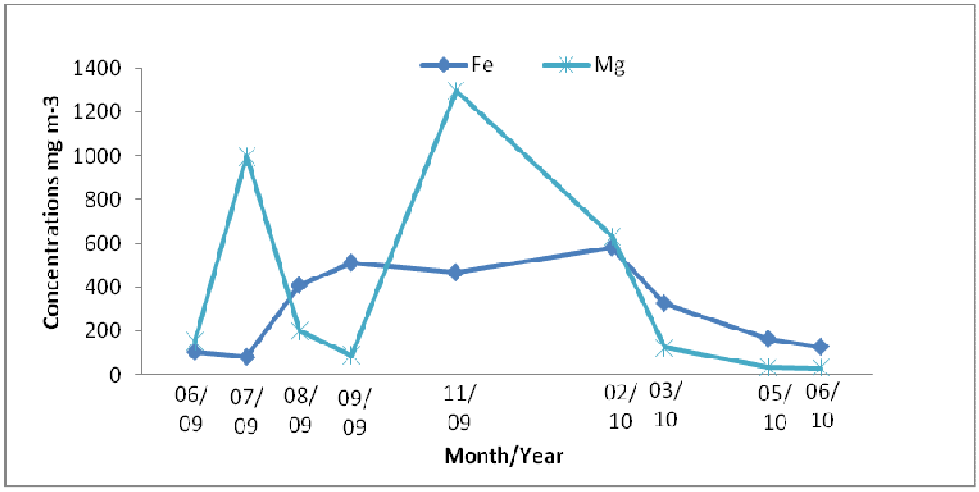

Figure 5- 87 Concentrations of Fe and Mg associated with suspended particles > 1.2 µm diameter in water from Luggie Burn water (mg m^{-3}).

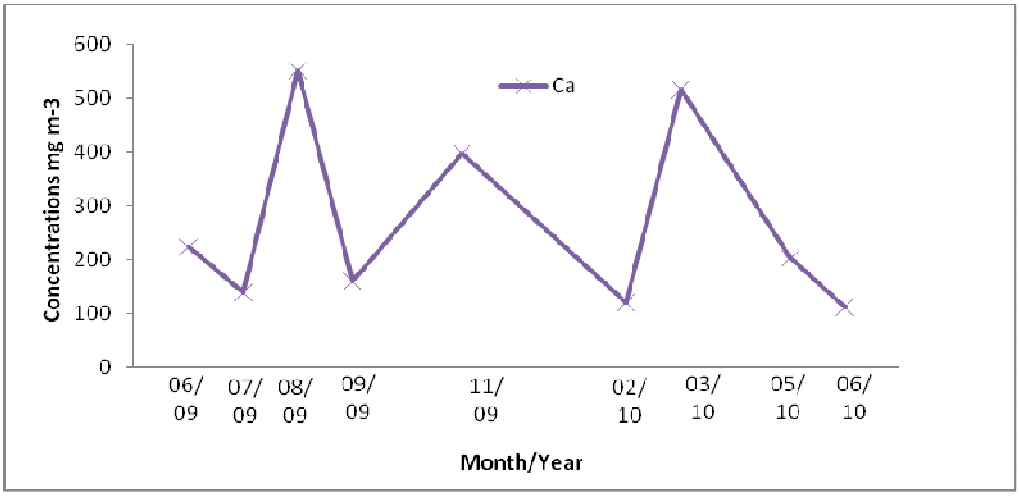

Figure 5- 88 Concentrations of Ca associated with suspended particles > 1.2 µm diameter in water from Luggie Burn water (mg m^{-3}).

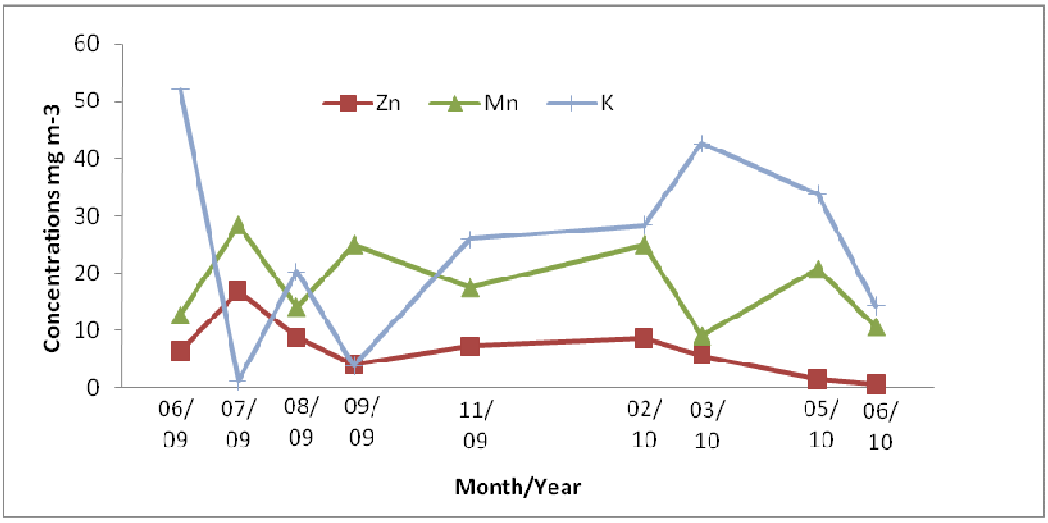

Figure 5- 89 Concentrations of K, Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Luggie Burn water (mg m^{-3}).

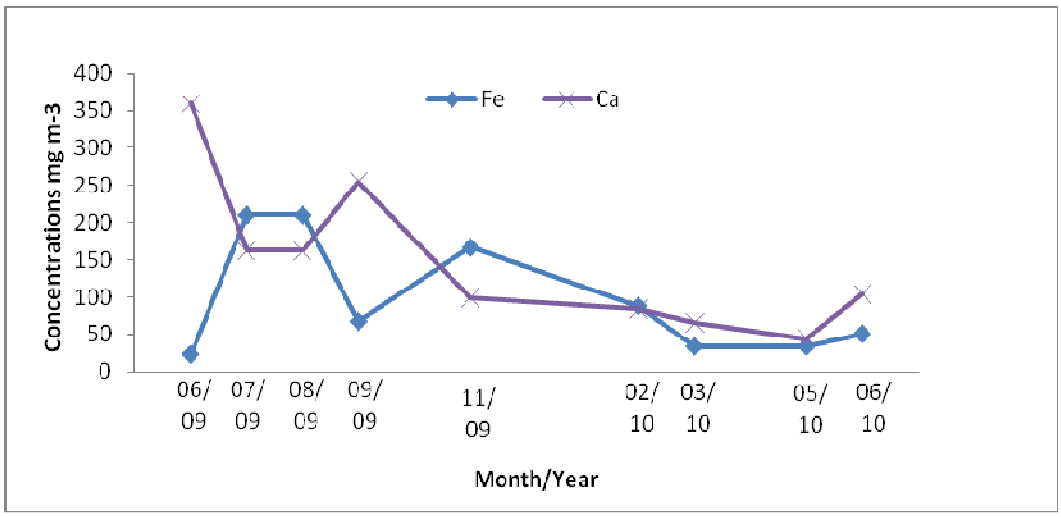

Figure 5- 90 Concentrations of Fe and Ca associated with suspended particles (1.2-0.2 µm) diameter in water from Luggie Burn water (mg m^{-3}).

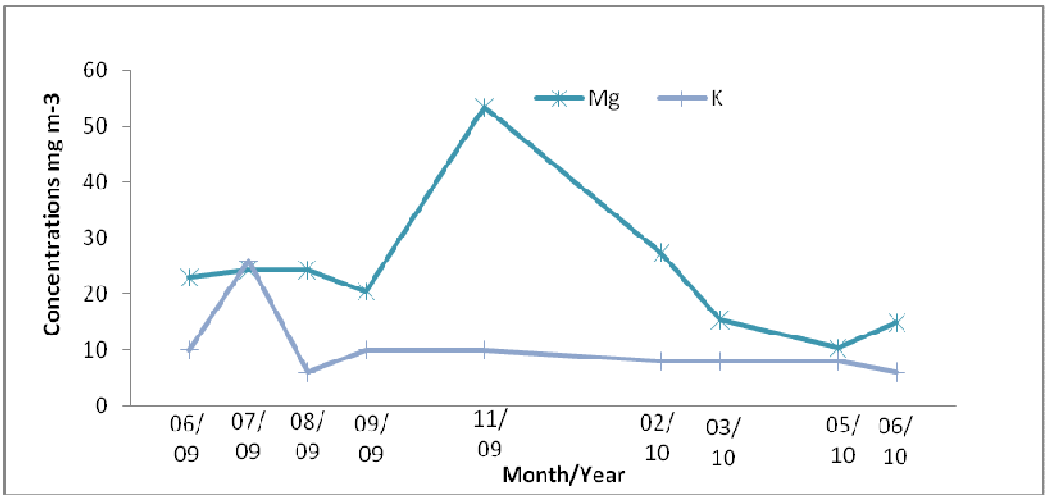

Figure 5- 91 Concentrations of K and Mg associated with suspended particles (1.2-0.2 µm) diameter in water from Luggie Burn water (mg m^{-3}).

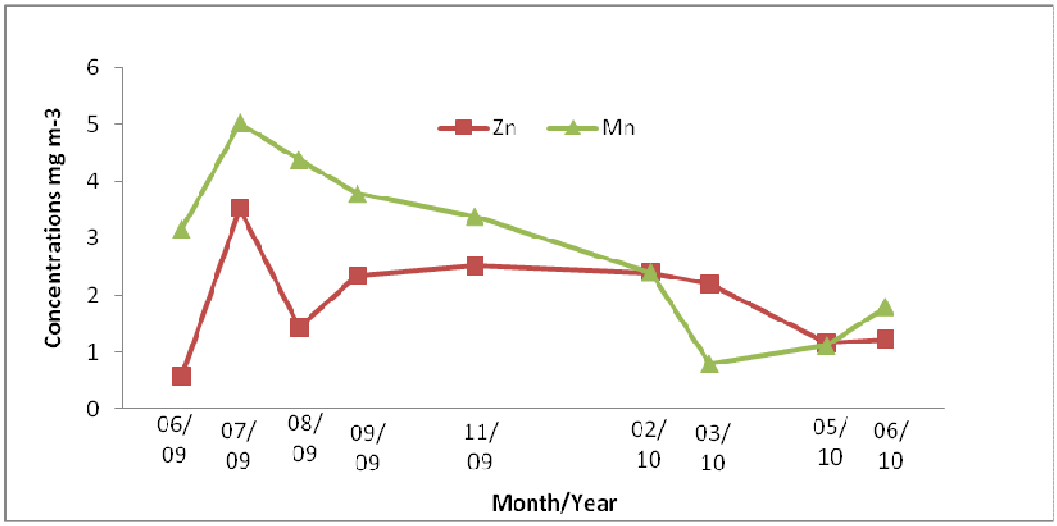

Figure 5- 92 Concentrations of Mn and Zn associated with suspended particles (1.2-0.2 µm) diameter in water from Luggie Burn water (mg m^{-3}).

Figures 5-93, 5-94 and 5-95 show the metal concentrations in sediment per unit volume of water in the > 1.2 μm fraction from Cameron Burn. The concentration trend was similar for Fe and Mn, where the greatest concentration was measured in September 2009, with the rising sediment mass. The concentration trend was similar for K and Zn and the highest concentration was observed in August 2009 whereas the greatest concentration of Ca and Mg was measured in June 2010. The figures also show the concentration of the five occasions of results to display an overall trend.

Figures 5-96, 5-97 and 5-98 show the metal concentrations in sediment per unit volume of water in the 1.2 μm to 0.2 μm fraction from Cameron Burn. The metal concentrations of sample months show different trends. On the other hand, the highest Ca concentration was measured on June 2009 and decreased with decreasing mass of sediment. Zn showed a regular concentration throughout the sampling months. The concentration trend is similar for Fe, K and Mg, where the greatest concentration was measured in June 2010 and increased with decreasing mass of sediment. The metal concentration in the >1.2 μm particles was higher than the metal concentration in the 1.2 μm to 0.2 μm fraction from Cameron Burn.

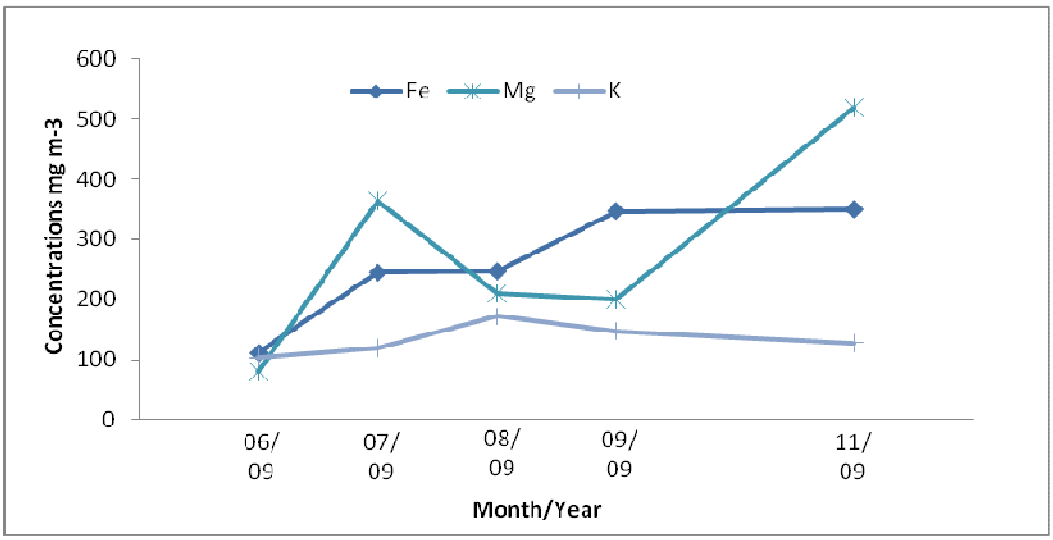

Figure 5- 93 Concentrations of K, Fe and Mg associated with suspended particles > 1.2 µm diameter in water from Cameron Burn water (mg m^{-3}).

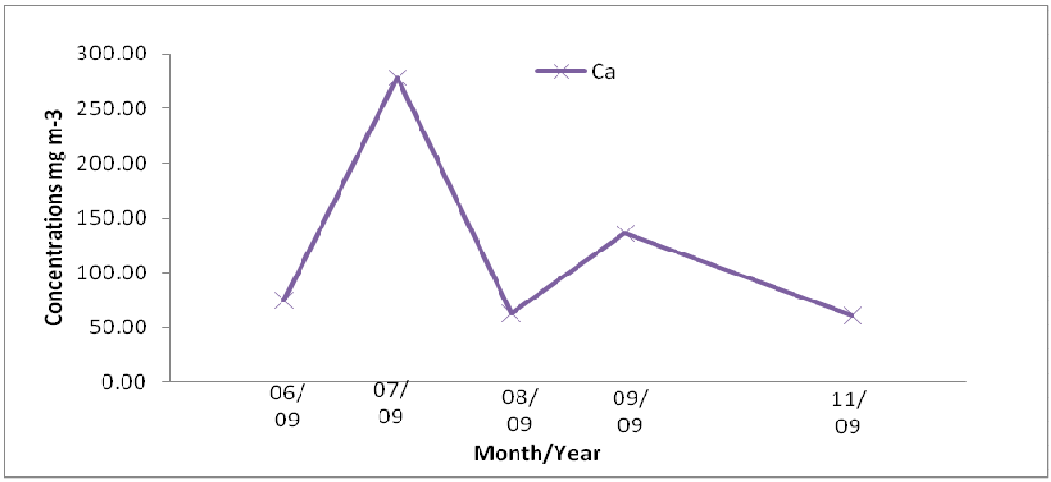

Figure 5- 94 Concentrations of Ca associated with suspended particles > 1.2 µm diameter in water from Cameron Burn water (mg m^{-3}).

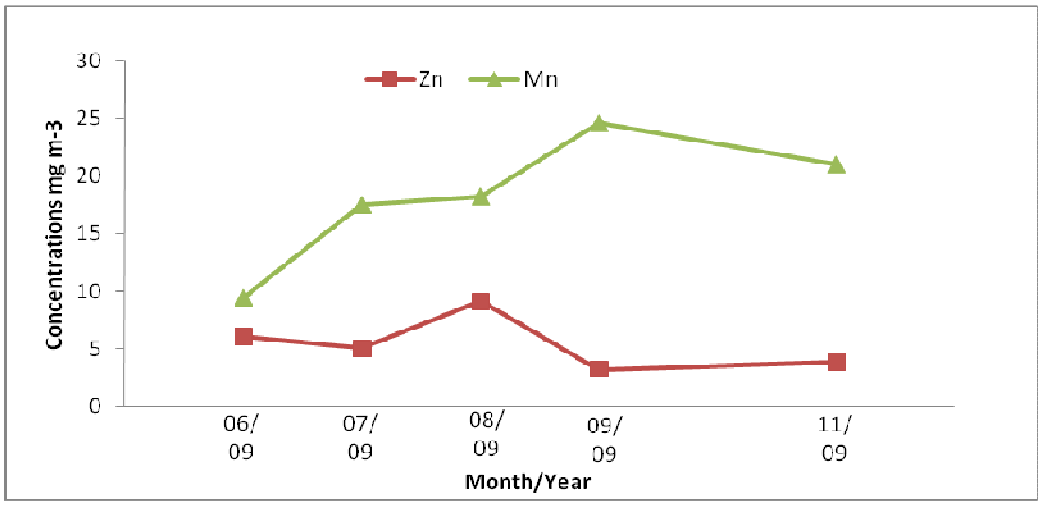

Figure 5- 95 Concentrations of Mn and Zn associated with suspended particles > 1.2 µm diameter in water from Cameron Burn water (mg m^{-3}).

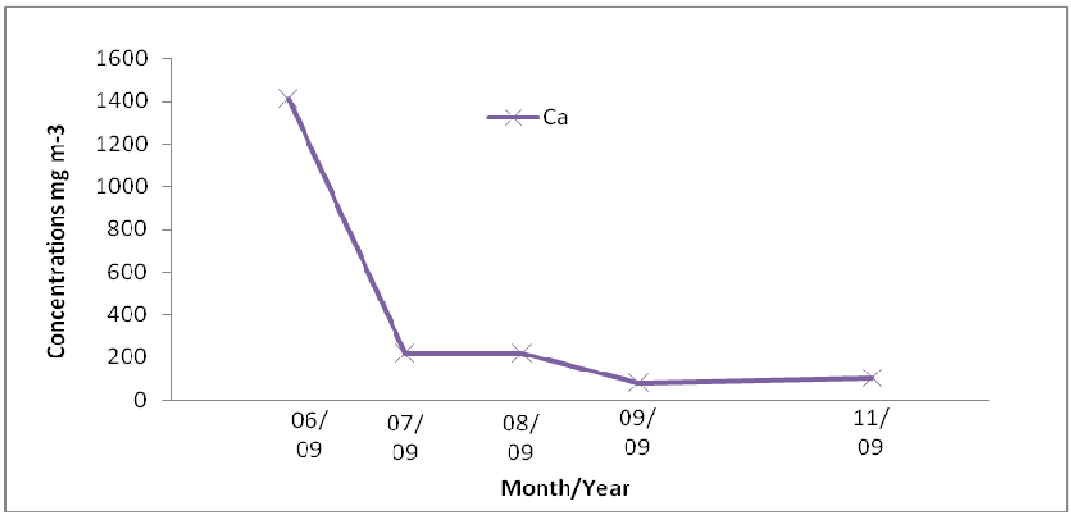

Figure 5- 96 Concentrations of Ca associated with suspended particles (1.2- 0.2 µm) diameter in water from Cameron Burn water (mg m^{-3}).

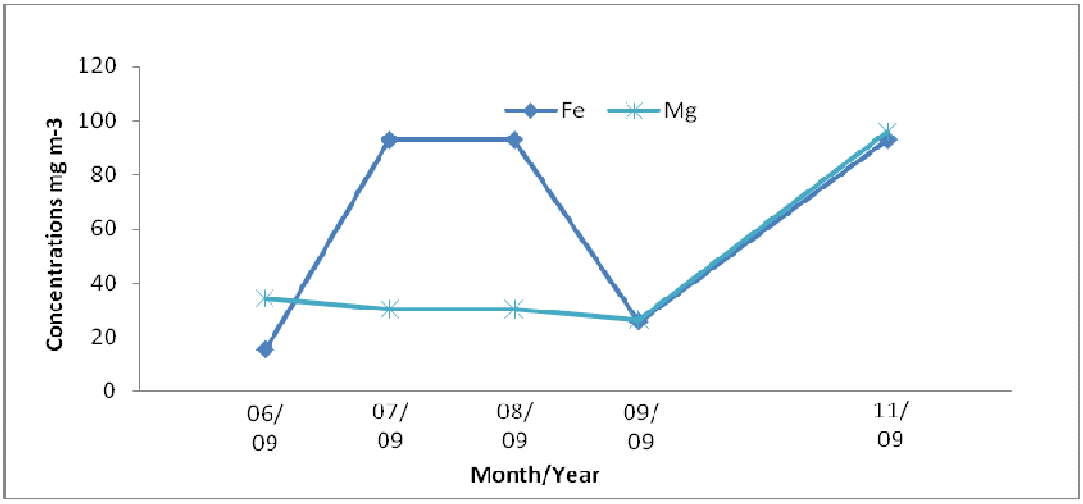

Figure 5- 97 Concentrations of Fe, Mg and associated with suspended particles (1.2- 0.2 µm) diameter in water from Cameron Burn water (mg m^{-3}).

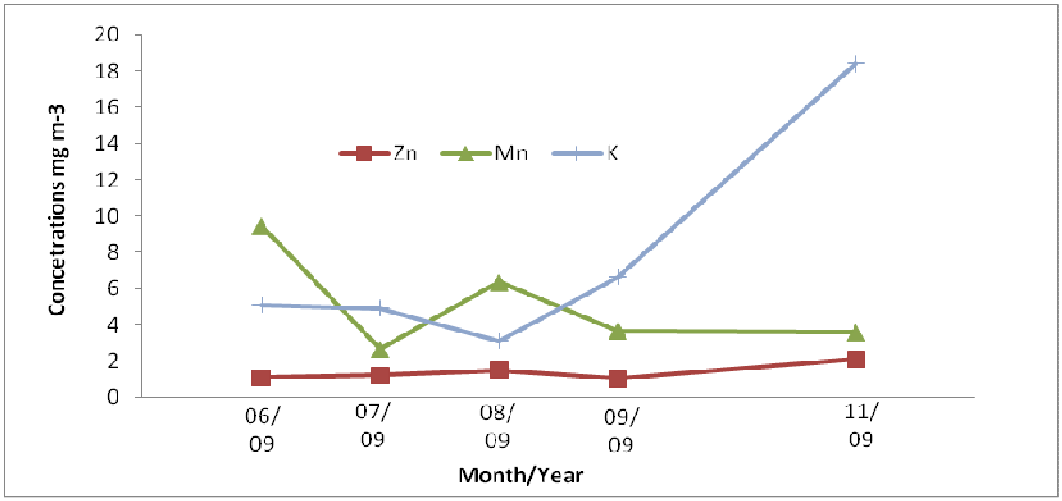

Figure 5- 98 Concentrations of K, Mn and Zn associated with suspended particles (1.2- 0.2 µm) diameter in water from Cameron Burn water (mg m^{-3}).

Figures 5-99, 5-100 and 5-101 show the metal concentrations in sediment per unit volume of water in the >1.2 μm fraction in water from the Cameron Burn. The metal concentrations in sediment per unit volume of water and the concentration in the suspended sediment showed similar trends for Ca and Mg. The metal concentrations also showed similar trends for Fe and K. The metal concentrations increased in July 2009 for Ca, Mg, Mn and Zn, with decreasing mass of sediment. A gradually decreasing change in metal concentration is then observed in August 2009 for Ca, Mg and Zn. On the other hand, the highest metals were measured in August 2009 for Fe and K with decreasing mass of sediment.

The ranges of the metal concentrations in sediment per unit volume of water in the range 1.2 μm to 0.2 μm from Cameron Burn are shown in figures 5-102, 5-103 and 5-104. The metal concentration showed a similar pattern for Ca and Mg with highest concentration measured in June 2009, increasing with increased mass of sediment. The highest metal concentration was measured in July 2009 for Mg and Mn. Metal concentrations for Fe and Zn were fairly constant in the summer 2009, and in winter and summer 2010.

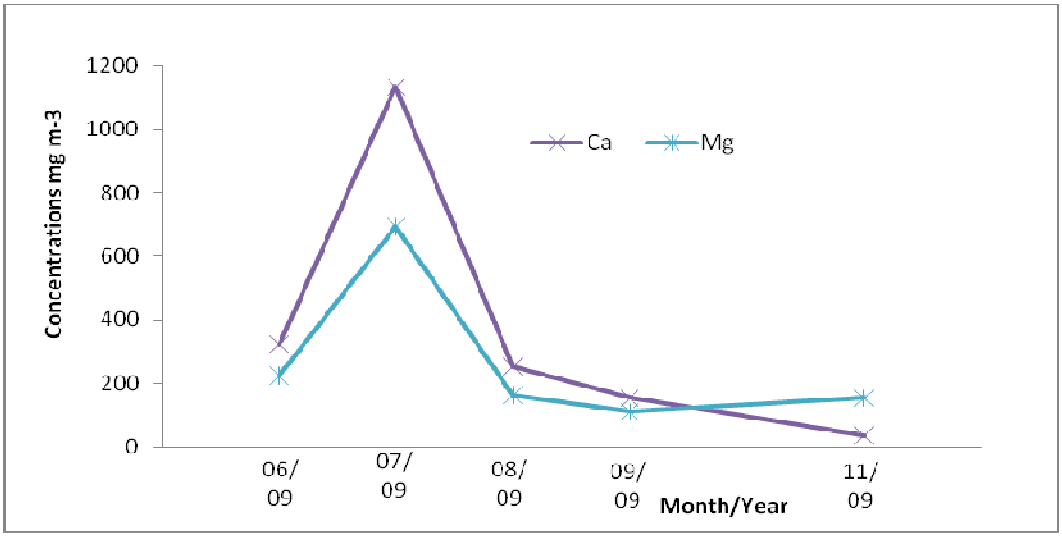

Figure 5- 99 Concentrations of Ca and Mg associated with suspended particles > 1.2 µm diameter in water from the Cameron Burn (mg m^{-3}).

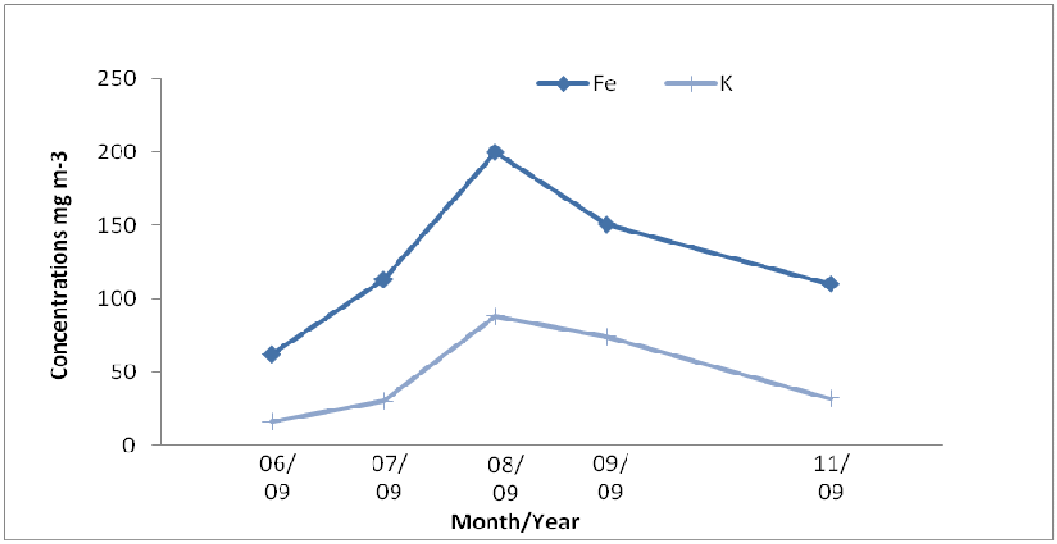

Figure 5- 100 Concentrations of Fe and K associated with suspended particles > 1.2 µm diameter in water from the Cameron Burn (mg m^{-3}).

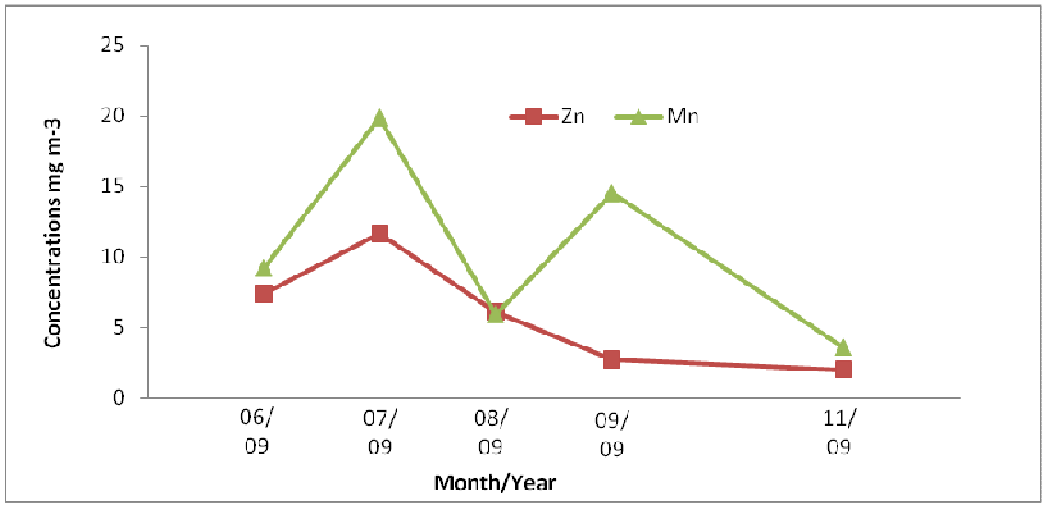

Figure 5- 101 Concentrations of Mn and Zn associated with suspended particles > 1.2 µm diameter in water from the Cameron Burn (mg m^{-3}).

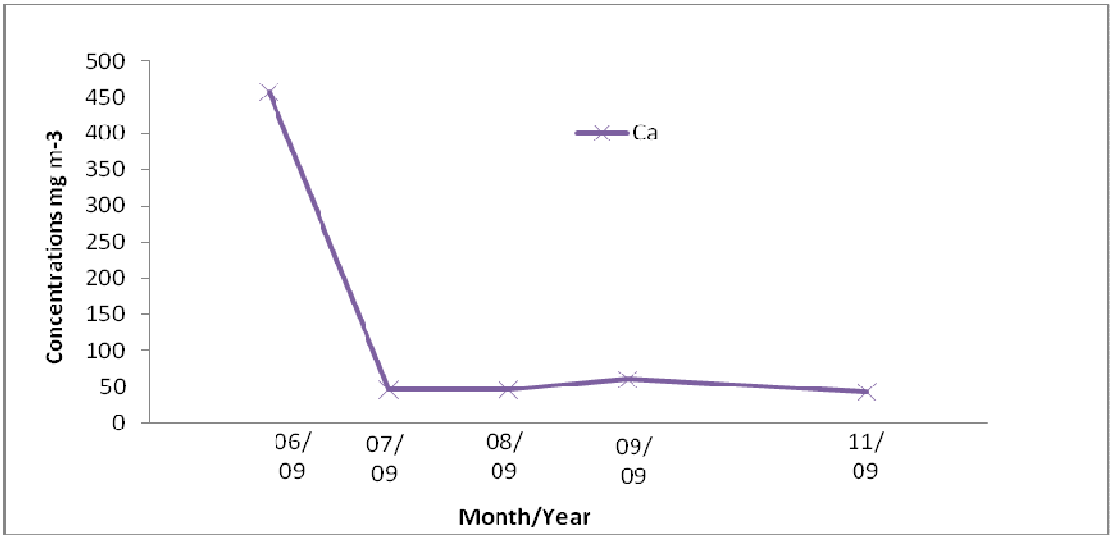

Figure 5- 102 Concentrations of Ca associated with suspended particles (1.2- 0.2 µm) diameter in water from the Cameron Burn (mg m^{-3}).

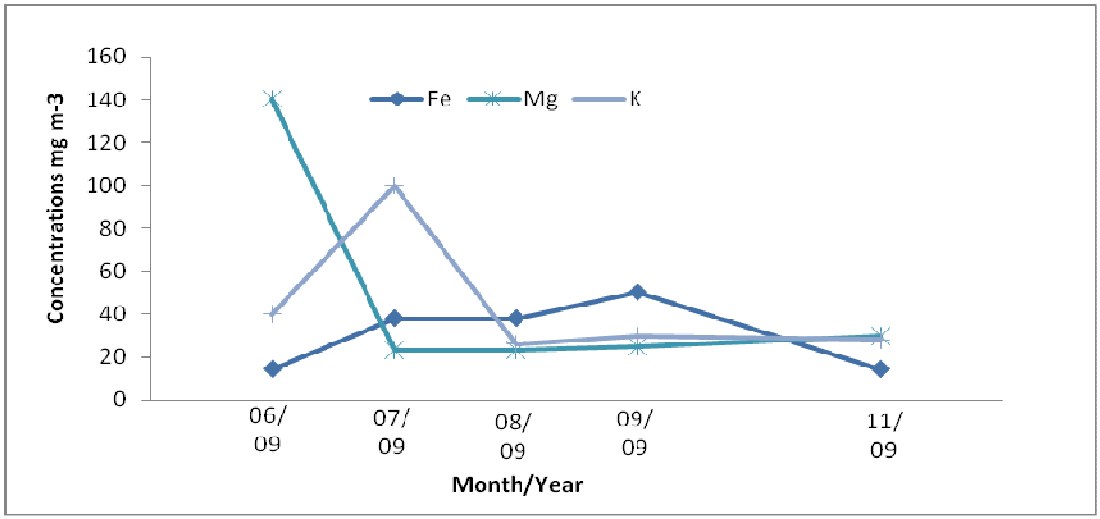

Figure 5- 103 Concentrations of Fe, K and Mg associated with suspended particles (1.2- 0.2 µm) diameter in water from the Cameron Burn (mg m^{-3}).

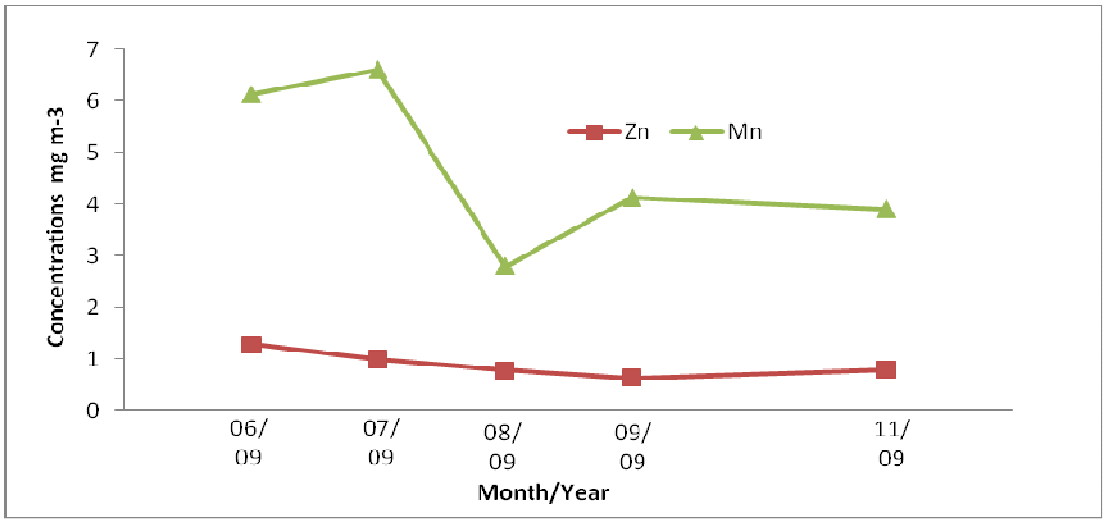

Figure 5- 104 Concentrations of Mn and Zn associated with suspended particles (1.2- 0.2 µm) diameter in water from the Cameron Burn (mg m^{-3}).

Table 5-24 Flux of metal (mg/s) from Allander water.

1.2 µm	Ca	Fe	K	Mg	Mn	Zn
June	14	12	3	14	1.8	0.7
July	100	55	23	161	7.2	2.8
August	423	549	100	317	15.1	13.6
September	97	67	16	62	5.0	2.3
November	658	305	57	640	15.3	3.2
February	148	26	26	134	1.4	0.9
March	239	56	54	47	2.5	1.9
May	43	8	6	8	0.4	0.3
June	7	16	3	1	2.6	0.0
1.2 - 0.2 µm						
June	6.4	3.6	0.4	1.1	0.3	0.1
July	14.7	20.4	1.6	4.8	2.4	0.7
August	70.6	303.4	3.3	15.8	5.0	1.5
September	17.6	25.8	1.0	4.6	1.9	0.8
November	78.2	79.4	17.5	21.4	5.3	3.8
February	10.2	10.2	0.7	4.0	0.4	0.9
March	14.4	7.7	1.6	2.3	0.2	1.1
May	6.5	2.6	1.5	0.8	0.0	0.3
June	4.5	4.1	4.7	0.6	0.2	0.4

Table 5-25 Flux of metal (mg/s) fromGlazert water.

1.2 µm	Ca	Fe	K	Mg	Mn	Zn
June	12	17.3	3	18	2	2.0
July	486	102.4	77	558	13	10.1
August	1581	822.9	231	914	31	36.0
September	65	137.6	5	52	15	2.9
November	568	617.8	60	432	21	2.3
February	251	108.0	27	178	3	1.7
March	171	190.4	27	11	3	4.8
May	55	44.8	12	11	4	0.7
June	156	161.6	13	34	6	1.2
1.2 - 0.2 µm						
June	11.5	20	1	2	1.6	0.06
July	53.0	70	5	14	7.3	1.96
August	228.7	404	14	48	142.5	3.26
September	37.3	54	1	6	12.3	1.22
November	95.2	103	9	27	23.3	6.65
February	16.1	48	1	6	2.8	0.67
March	68.4	31	23	7	6.5	4.56
May	7.7	35	1	1	3.9	0.47
June	14.9	128	1	1	6.5	0.72

Table 5-26 Flux of metal (mg/s) from Bothlin Burn.

1.2 µm	Ca	Fe	K	Mg	Mn	Zn
June	5.2	7.1	1.5	6	0.8	0.4
July	84.4	783.3	44.9	324	30.1	4.9
August	3770.0	1257.0	384.5	625	54.1	33.2
September	225.2	407.0	52.2	107	16.3	3.5
November	225.4	671.8	133.4	1208	26.5	7.8
February	715.3	220.2	59.0	264	9.8	3.8
March	115.1	150.3	31.5	41	9.6	2.1
May	40.2	35.0	11.2	6	3.5	0.2
June	28.5	55.6	1.6	7	7.7	0.1
1.2 - 0.2 µm						
June	13.5	4.8	0.5	1.5	0.3	0.12
July	30.3	20.7	3.9	10.5	1.4	0.84
Auqust	432.5	562.3	10.7	65.0	13.4	2.99
September	45.9	18.1	1.7	6.7	2.0	1.07
November	88.9	160.5	6.9	30.1	3.7	1.93
February	55.8	82.5	3.1	11.2	0.9	1.10
March	22.1	14.6	1.8	2.9	0.2	0.97
May	19.9	17.3	0.9	1.6	0.1	0.25
June	20.2	15.8	3.3	2.4	0.5	0.72

Table 5-27 Flux of metal (mg/s) from Luggie Burn.

1.2 µm	Ca	Fe	K	Mg	Mn	Zn
June	32.6	15	7	22	1.9	0.95
July	447.6	26	5	321	9.2	5.45
August	2128.4	1578	355	777	54.6	33.89
September	70.2	225	13	39	11.0	1.80
November	668.6	783	353	2177	29.4	12.16
February	562.8	272	65	296	11.7	4.08
March	264.2	167	47	63	4.6	2.92
May	48.2	39	11	9	4.9	0.35
June	37.0	43	7	11	3.5	0.19
1.2 - 0.2 µm						
June	52.5	3.3	1	3.3	0.5	0.08
July	52.2	67.8	8	7.8	1.6	1.13
Auqust	625.3	812.9	23	94.0	16.9	5.56
September	112.0	29.6	4	9.0	1.7	1.03
November	165.6	280.6	17	89.7	5.7	4.23
February	39.2	41.3	4	12.9	1.1	1.13
March	33.6	17.2	4	7.9	0.4	1.13
May	10.6	8.1	2	2.4	0.3	0.28
June	34.7	16.8	2	4.9	0.6	0.41

Table 5-18 to 5-21 shows the metal fluxes in the > 1.2 fraction and in the range 1.2 - 0.2 µm from Allander, Glazert Bothlin and Luggie in the sampling months. The metal fluxes show similar trends, where metal flux increases with increasing flow rate and decreases with decreased flow rate. The metal fluxes were higher in the summer of 2009 (July and August), in autumn 2009 (November) and winter 2010 (February and March). The metal fluxes started to decrease in summer 2010 (May and June). The metal flux may be related to the type of particle that dominates in the river at different times of the year. In the times of low metal flux, it may be that the finer particles dominate, because flows will generally be lower. In winter and early spring, the flows will tend to be greater and so there is likely to be coarser particles, which have lower concentrations of the elements being measured. So there is an overall cycle, and the fine detail of river flows seems secondary to this.

On the other hand, in the > 1.2 µm fraction in the Allander and Glazert water high concentration in the suspended sediment and high fluxes were measured for Fe, K, Mn and Zn in August 2009. In the Allander water in the > 1.2 µm fraction high concentrations for Ca and Mg in the suspended sediment were measured in November 2009, while all metal fluxes were high with high flow rate. On the other hand, low concentrations of metal in the suspended sediment were measured in November in the > 1.2 µm fraction, while high metal fluxes were measured in the Glazert water. In the 1.2 - 0.2 µm fraction high metal flux was measured in August in the Allander and Glazert water, in contrast low metal concentrations were measured in the suspended sediment. In Allander in the 1.2 - 0.2 µm fraction high metal concentrations in the sediment and high metal flux were measured in November 2009. While in the 1.2 - 0.2 µm fraction in Glazert water low metal concentrations in the sediment and high metal flux were measured in November 2009. In the 1.2 - 0.2 µm fraction low metal flux and low metal concentrations were measured in the suspended sediment in February 2010 in the Allander and Glazert water.

In addition, in the > 1.2 µm fraction in August 2009 high concentration in the suspended sediment and high fluxes were measured in the Bothlin Burn. In the Luggie Burn in the > 1.2 µm fraction high concentrations for Ca and Fe in the suspended sediment were measured in August 2009, while all metals fluxes were high with high flow rate. On the other hand, high metal fluxes and low concentrations of metal in the suspended sediment were measured in November in the > 1.2 µm fraction, in both tributaries. In the Bothlin and Luggie Burn in the > 1.2 µm and in the 1.2 - 0.2 µm fractions high concentrations of metal in the suspended sediment and high metal fluxes were measured in February 2010. In the 1.2 - 0.2 µm fraction high metal flux was measured in August in the Bothlin and

Luggie Burn, in contrast low metal concentrations were measured in the suspended sediment. In Bothlin and Luggie Burn in the 1.2 - 0.2 µm fraction high metal concentrations in the sediment and high metal flux were measured in November 2009. The overall results indicated that there is no strong relationship between the metal concentrations in suspended sediment and the amount of flux transport in the river.

5.3.1 Discussion

The results show a different effect of the mass of sediment and concentrations of metals in suspended sediment and with the metal concentrations in sediment per unit volume of water. Some factors can affect the increase or decrease in mass of sediment in the river such as the time of flow rate, the rainfall amount and the size of suspended sediment. These factors can affect the increase or decrease in metal in the suspended sediment and the metal concentrations in sediment per unit volume of water. For example increased mass of sediment in July 2009 and June 2010 in the >1.2 μm fraction from Craigton Burn caused decreased metal concentration in the suspended sediment and increased the metal concentrations in sediment per unit volume of water. In addition, increased mass of sediment in November 2009 in the >1.2 μm fraction from Craigmaddie caused decreases in the metal concentration in the suspended sediment and decreased the metal concentrations in sediment per unit volume of water. That may be because the mass of sediment contains metals not measured in the current study.

The increase in mass of sediment in May and June 2010 in the >1.2 μm fraction from Glazert Water caused increases in the metal concentration in the suspended sediment and increased the metal concentrations in sediment per unit volume of water. On the other hand, in the >1.2 μm fraction from Allander water decreased mass of sediment in August 2009 and February 2010 caused increases of the metal concentration in the suspended sediment and increased the metal concentrations in sediment per unit volume of water. In the 1.2 μm to 0.2 μm fraction from Craigmaddie decreased mass of sediment cause decreases in the metal concentration of the suspended sediment and decreased the metal concentrations in sediment per unit volume of water which may be because a small amount of metal concentrations were associated with suspended sediment.

The overall result shows that there is no strong relationship between the flow rate and the metal concentrations in sediment per unit volume of water. Increased flow rate does not always cause an increase in the metal concentrations in sediment per unit volume of water. In addition, decreased flow rate does not always cause the metal concentrations to increase or decrease in sediment per unit volume of water.

Based on data from the Centre for Ecology and Hydrology National River Flow Archive (See Appendix 2), the Allander water at Milngave has a mean flow of 1.317 $m^3 s^{-1}$. The metal load in the > 1.2 μm fraction and the mean flow is taken together to give the following estimates of different metals: 9400 kg Ca, 4200 kg Fe, 1700 kg K, 7200 kg Mg, 380 kg Mn and 150kg Zn per year are transported in the > 1.2 μm fraction.

Regarding the 1.2-0.2 μm fraction, it was found that approximately 1400 kg Ca, 1400 kg Fe, 260 kg K, 300 kg Mg, 96 kg Mn and 66 kg Zn per year are transported in this fraction. This shows that there are considerable amounts of metals load transported by the Allander water to River Kelvin in both size fractions.

Glazert water at Milton Campsite has a mean flow of 2.081 $m^3 s^{-1}$. Referring to the results in the > 1.2 μm fraction, using the metal loads in these fractions given above, and the mean flow, it was found that approximately 1500 kg Ca, 1100 kg Fe, 1900 kg K, 9000 kg Mg, 660 kg Mn and 280 kg Zn per year were transported in the > 1.2 μm fraction.

Referring to the results in the 1.2-0.2 μm fraction, it was found that approximately 2500 kg Ca, 7002 kg Fe, 230 kg K, 400 kg Mg, 700 kg Mn and 90 kg Zn per year are transported in the range 1.2-0.2 μm. The results show that there are considerable amounts of metals load transported by the Glazert water.

The Bothlin Burn at Auchengeich has a mean flow of 0.773 $m^3 s^{-1}$. Referring to the results in the > 1.2 μm fraction, using the metal loads in these fractions given above, and the mean flow, it was found that approximately 1200 kg Ca, 2000 kg Fe, 1700 kg K, 8400 kg Mg, 680 kg Mn and 1570 kg Zn per year are transported in the low > 1.2 μm fraction. Referring to the results in the 1.2-0.2 μm fraction using the metal loads in these fractions given above, and the mean flow, it was found that approximately 2400 kg Ca, 2200 kg Fe, 150 kg K, 400 kg Mg, 60 kg Mn and 40 kg Zn per year are transported in the range 1.2-0.2 μm fraction. This shows that there were considerable amounts of metals load transported by the Bothlin Burn to River Kelvin.

The Luggie Burn at Auchengeich has a mean flow of 0.872 $m^3 s^{-1}$. Referring to the results in the > 1.2 μm fraction, using the metal loads in these fractions given above, and the mean flow, it was found that approximately 1200 kg Ca, 7600 kg Fe, 1900 kg K, 9800 kg Mg, 450 kg Mn and 160 kg Zn per year are transported in the > 1.2 μm fraction. Referring to the results in the 1.2-0.2 μm fraction, there is about 3700 kg Ca, 2400 kg Fe, 250 kg K, 590 kg Mg, 70 kg Mn and 50 kg Zn per year transported in the 1.2-0.2 μm fraction.

5.3.2 Conclusion

The results have given information on the amount of transport in the River Kelvin and it is tributaries for Ca, Fe, K, Mg, Mn and Zn. The results in this section have shown that there is a considerable amount of metals transport within the water of the tributaries. There are some similar trends of the metal concentrations between two size fractions in the same site and also in different sampling sites. The concentration trend is similar in the > 1.2 µm diameter for Ca in the Craigtion Burn and Luggie Burn. In addition, the concentrations trend is similar in the > 1.2 µm fraction for Zn in the Allander Water, and Craigmaddie Burn. Mn concentration trend is similar in the > 1.2 µm diameter fraction in Craigtion Burn and Allander Burn. The concentration trend was similar in the > 1.2 µm diameter for Mg in the Bothlin Burn and Luggie Burn. The concentration trend was similar in the > 1.2 µm diameter fraction for Mg in the Allander water, Craigmaddie Burn and Glazert. On the other hand, the concentration trend was similar in the 0.2 -1.2- µm diameters fraction for Mg in the Craigton Burn, and Allander Burn. In addition, the concentration trend was similar in the 0.2 -1.2 µm diameter fraction for Fe in the Craigton Burn, and Allander Burn.

Overall results show that there are considerable amounts of metals load transported in different tributaries of the River Kelvin. The results show the large metals load transport in the large fraction was higher than that transport in the fine fraction. Based on the sediment results and utilizing data from the Centre for Ecology and Hydrology National River Flow Archive for average flow loading information, the result indicated that considerable metal loads per year were transported in the > 1.2 µm and in the 0.2 – 1.2 µm fractions in the Kelvin River.

6 Conclusions and Future work

6.1 Conclusions

The main objective of the current research study was to investigate the role of the suspended sediment in metal transport from River Kelvin and it is tributaries. The investigation was carried out to study the concentration of metal in suspended sediment at different sampling sites and in different months. The research firstly concluded that filter papers and micro-fiber membrane filters are contaminated by different concentrations of metals. It revealed unacceptable concentrations of metals in some filter papers used. The concentrations of the contamination elements were corrected for, by subtracting the contaminated concentration, measured in the digested blank filter paper, from the total concentrations measured in the digested suspended sediments from the river samples.

The ability of selected components of suspended material to take up heavy metals from water was studied. This assessed the take up of heavy metals in sample adsorption systems and the influence of the mixed systems of clays, humic material and iron oxide. The results indicated that the adsorption capacity of bentonite exceeds that of the other components, which was similar to that previously reported by Garcia (1978).

In the mixed system the results indicate that the K_d values were different for each metal. In general the K_d values were different, under the same conditions of fixed concentrations and different mixed material weights. This is an important observation, which suggests that in studies of natural systems the use of Kd values for individual sorbent materials may not be valid. It may be more appropriate to assess metal uptake based on likely mixtures of materials that actually exist in the natural systems.

The result of the seven tributaries survey provided an overview on the concentrations of Ca, Fe, K, Mg, Mn and Zn in the suspended sediment along the course of the River Kelvin. Using the mean flow from the Centre for Ecology and Hydrology National River Flow Archive shows that a large amount of metal is transferred in the <1.2 μm and in the 1.2-0.2 μm fraction in a year. The overall result shows there is no strong relationship between the flow rate and in the metal in the suspended sediment and the metal concentrations in the weight of sediment per unit volume of water.

6.2 Future Work

The research has provided an overview of the impact of suspended sediment for the transfer of metals the environment. With the completion of this research work, however, many suggestions for future action were found. The recommendations include that the work can be done in laboratory studies and field studies.

It would be interesting to investigate contamination from membrane filters further. The investigation should look for different techniques to collect suspended sediment. It would also be interesting to investigate the ability of different mixed components to take up metals. The investigation should look at what parameters control sorption, for example the effect of pH. In the field, the investigation on the role of nanoparticles to transport metals in the suspended sediment also needs to use a new analytical technique such as ICP-MS with low detection limits. In addition, more regular sampling and detailed measurement of parameters such as pH, flow rate of each river is required and a survey of the origin of the sediment and land use in the catchments and inputs from road salting and gritting during the winter months.

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APPENDICES

Appendix 1

Daily rainfall amount in sampling months 2009 Glasgow area determine from Glasgow University (Dr. T. H. Flowers).

Day	June	July	August	September	October	November
Saturday			1 1			
Sunday			2 0			1 20
Monday	1 0		3 1			2 1
Tuesday	2 0		4 1	1 1		3 3
Wednesday	3 0	1 0	5 0	2 13		4 11
Thursday	4 0	2 0	6 0	3 3	1 2	5 1
Friday	5 0	3 21	7 0	4 1	2 9	6 6
Saturday	6 0	4 0	8 0	5 0	3 0	7 1
Sunday	7 0	5 1	9 10	6 5	4 0	8 0
Monday	8 0	6 11	10 0	7 19	5 0	9 4
Tuesday	9 0	7 0	11 2	8 6	6 2	10 0
Wednesday	10 0	8 0	12 0	9 0	7 0	11 3
Thursday	11 0	9 0	13 0	10 0	8 0	12 0
Friday	12 0	10 0	14 31	11 0	9 0	13 10
Saturday	13 0	11 12	15 2	12 0	10 8	14 1
Sunday	14 0	12 0	16 6	13 0	11 0	15 0
Monday	15 4	13 7	17 1	14 0	12 0	16 6
Tuesday	16 3	14 3	18 1	15 0	13 0	17 7
Wednesday	17 5	15 3	19 15	16 0	14 0	18 19
Thursday	18 8	16 0	20 18	17 0	15 0	19 38
Friday	19 1	17 1	21 2	18 0	16 0	20 1
Saturday	20 0	18 0	22 4	19 0	17 0	21 5
Sunday	21 0	19 2	23 3	20 0	18 3	22 14
Monday	22 0	20 1	24 0	21 0	19 2	23 6
Tuesday	23 0	21 7	25 4	22 0	20 3	24 15
Wednesday	24 0	22 0	26 8	23 0	21 0	25 15
Thursday	25 0	23 0	27 4	24 0	22 0	26 7
Friday	26 0	24 0	28 2	25 0	23 5	27 1
Saturday	27 0	25 6	29 0	26 0	24 9	28 1
Sunday	28 0	26 2	30 9	27 0	25 2	29 0
Monday	29 0	27 0	31 14	28 0	26 1	30 0
Tuesday	30 0	28 12		29 4	27 11	
Wednesday		29 0		30 2	28 0	
Thursday		30 0			29 4	
Friday		31 2			30 13	
Saturday					31 6	
Total	21	91	140	54	80	195

Daily rainfall amount in sampling months 2010 Glasgow area determine from Glasgow University (Dr. T. H. Flowers).

Day	February	March	April	May	June
Saturday				1 0	
Sunday				2 1	
Monday	1 2	1 0		3 0	
Tuesday	2 2	2 0		4 0	1 2
Wednesday	3 0	3 0		5 2	2 0
Thursday	4 3	4 0	1 0	6 2	3 0
Friday	5 7	5 0	2 8	7 0	4 0
Saturday	6 0	6 0	3 1	8 0	5 0
Sunday	7 0	7 0	4 5	9 0	6 0
Monday	8 0	8 0	5 15	10 0	7 2
Tuesday	9 0	9 0	6 8	11 0	8 10
Wednesday	10 0	10 0	7 0	12 0	9 0
Thursday	11 0	11 0	8 0	13 5	10 0
Friday	12 0	12 0	9 0	14 1	11 0
Saturday	13 0	13 0	10 0	15 2	12 0
Sunday	14 1	14 0	11 0	16 0	13 2
Monday	15 2	15 0	12 0	17 0	14 0
Tuesday	16 0	16 1	13 0	18 0	15 0
Wednesday	17 0	17 0	14 0	19 0	16 0
Thursday	18 0	18 2	15 0	20 0	17 0
Friday	19 0	19 0	16 0	21 0	18 0
Saturday	20 0	20 0	17 0	22 0	19 0
Sunday	21 0	21 2	18 0	23 0	20 0
Monday	22 2	22 3	19 0	24 0	21 0
Tuesday	23 1	23 0	20 0	25 0	22 0
Wednesday	24 26	24 4	21 0	26 0	23 0
Thursday	25 12	25 11	22 0	27 0	24 0
Friday	26 6	26 0	23 0	28 0	25 0
Saturday	27 1	27 0	24 0	29 4	26 0
Sunday	28 0	28 9	25 0	30 2	27 5
Monday		29 20	26 0		28 3
Tuesday		30 11	27 0		29 0
Wednesday		31 0	28 0		30 2
Thursday			29 2		
Friday			30 0		
Saturday			31 4		
Total	65	53	43	54	

Appendix 2

Daily flow rate Allander water (SEAPA)

Station name: Milngavie, Station number: 133113, External number: 84026
River: Allander Water, Operator: SEPA, Easting: 255850, Northing: 673559

01/06/09	0.182	01/07/09	0.084	01/08/09	0.841	01/09/09	3.143	01/11/09	8.319
02/06/09	0.151	02/07/09	0.078	02/08/09	0.646	02/09/09	2.868	02/11/09	4.315
03/06/09	0.133	03/07/09	0.521	03/08/09	0.46	03/09/09	3.763	03/11/09	5.546
04/06/09	0.125	04/07/09	0.255	04/08/09	0.46	04/09/09	1.695	04/11/09	2.948
05/06/09	0.129	05/07/09	0.17	05/08/09	0.375	05/09/09	1.811	05/11/09	1.977
06/06/09	0.118	06/07/09	0.174	06/08/09	0.279	06/09/09	3.255	06/11/09	1.956
07/06/09	0.107	07/07/09	0.155	07/08/09	0.228	07/09/09	3.813	07/11/09	1.34
08/06/09	0.124	08/07/09	0.123	08/08/09	0.206	08/09/09	8.468	08/11/09	0.934
09/06/09	0.117	09/07/09	0.113	09/08/09	0.255	09/09/09	2.389	09/11/09	0.887
10/06/09	0.102	10/07/09	0.108	10/08/09	0.463	10/09/09	1.391	10/11/09	1.17
11/06/09	0.093	11/07/09	0.18	11/08/09	0.347	11/09/09	0.979	11/11/09	0.879
12/06/09	0.081	12/07/09	0.235	12/08/09	0.296	12/09/09	0.745	12/11/09	1.151
13/06/09	0.111	13/07/09	0.329	13/08/09	0.242	13/09/09	0.579	13/11/09	1.392
14/06/09	0.09	14/07/09	0.39	14/08/09	7.351	14/09/09	0.487	14/11/09	2.492
15/06/09	0.108	15/07/09	0.329	15/08/09	4.017	15/09/09	0.416	15/11/09	1.173
16/06/09	0.114	16/07/09	0.251	16/08/09	1.666	16/09/09	0.373	16/11/09	2.194
17/06/09	0.475	17/07/09	0.205	17/08/09	1.43	17/09/09	0.323	17/11/09	3.6
18/06/09	0.334	18/07/09	0.178	18/08/09	1.701	18/09/09	0.296	18/11/09	4.062
19/06/09	0.254	19/07/09	0.146	19/08/09	7.211	19/09/09	0.281	19/11/09	12.926
20/06/09	0.198	20/07/09	0.147	20/08/09	6.692	20/09/09	0.264	20/11/09	5.332
21/06/09	0.164	21/07/09	0.252	21/08/09	2.891	21/09/09	0.51	21/11/09	3.364
22/06/09	0.151	22/07/09	0.491	22/08/09	2.183	22/09/09	0.442	22/11/09	2.835
23/06/09	0.13	23/07/09	0.38	23/08/09	4.976	23/09/09	0.362	23/11/09	2.646
24/06/09	0.116	24/07/09	0.284	24/08/09	2.08	24/09/09	0.329	24/11/09	6.979
25/06/09	0.105	25/07/09	0.219	25/08/09	1.295	25/09/09	0.308	25/11/09	6.175
26/06/09	0.098	26/07/09	0.473	26/08/09	2.975	26/09/09	0.281	26/11/09	5.811
27/06/09	0.103	27/07/09	0.375	27/08/09	2.034	27/09/09	0.278	27/11/09	3.568
28/06/09	0.1	28/07/09	1.234	28/08/09	1.472	28/09/09	0.319	28/11/09	1.99
29/06/09	0.093	29/07/09	0.85	29/08/09	1.042	29/09/09	0.381	29/11/09	1.304
30/06/09	0.087	30/07/09	0.458	30/08/09	1.974	30/09/09	0.412	30/11/09	0.996
		31/07/09	0.472	31/08/09	4.673				

Daily flow rate Allander water (SEAPA)

01/02/2010	0.494	01/03/2010	0.560	01/05/2010	0.224	01/06/2010	0.172
02/02/2010	0.641	02/03/2010	0.477	02/05/2010	0.204	02/06/2010	0.142
03/02/2010	0.49	03/03/2010	0.412	03/05/2010	0.194	03/06/2010	0.136
04/02/2010	0.712	04/03/2010	0.373	04/05/2010	0.189	04/06/2010	0.132
05/02/2010	0.923	05/03/2010	0.508	05/05/2010	0.187	05/06/2010	0.129
06/02/2010	0.881	06/03/2010	0.654	06/05/2010	0.183	06/06/2010	0.128
07/02/2010	0.664	07/03/2010	0.609	07/05/2010	0.172	07/06/2010	0.128
08/02/2010	0.54	08/03/2010	0.456	08/05/2010	0.168	08/06/2010	0.18
09/02/2010	0.445	09/03/2010	0.385	09/05/2010	0.166	09/06/2010	0.162
10/02/2010	0.371	10/03/2010	0.347	10/05/2010	0.162	10/06/2010	0.144
11/02/2010	0.348	11/03/2010	0.372	11/05/2010	0.16	11/06/2010	0.139
12/02/2010	0.316	12/03/2010	0.352	12/05/2010	0.159	12/06/2010	0.136
13/02/2010	0.295	13/03/2010	0.316	13/05/2010	0.199	13/06/2010	0.137
14/02/2010	0.311	14/03/2010	0.304	14/05/2010	0.198	14/06/2010	0.136
15/02/2010	0.522	15/03/2010	0.285	15/05/2010	0.183	15/06/2010	0.133
16/02/2010	0.36	16/03/2010	0.255	16/05/2010	0.18	16/06/2010	0.132
17/02/2010	0.29	17/03/2010	0.291	17/05/2010	0.174	17/06/2010	0.126
18/02/2010	0.253	18/03/2010	0.345	18/05/2010	0.169	18/06/2010	0.122
19/02/2010	0.232	19/03/2010	0.394	19/05/2010	0.169	19/06/2010	0.12
20/02/2010	0.268	20/03/2010	0.274	20/05/2010	0.167	20/06/2010	0.119
21/02/2010	0.269	21/03/2010	0.244	21/05/2010	0.164	21/06/2010	0.118
22/02/2010	0.243	22/03/2010	0.701	22/05/2010	0.160	22/06/2010	0.118
23/02/2010	0.232	23/03/2010	0.488	23/05/2010	0.155	23/06/2010	0.117
24/02/2010	0.345	24/03/2010	0.833	24/05/2010	0.148	24/06/2010	0.116
25/02/2010	2.021	25/03/2010	0.817	25/05/2010	0.143	25/06/2010	0.114
26/02/2010	1.433	26/03/2010	2.369	26/05/2010	0.141	26/06/2010	0.113
27/02/2010	0.997	27/03/2010	0.991	27/05/2010	0.140	27/06/2010	0.12
28/02/2010	0.711	28/03/2010	0.845	28/05/2010	0.140	28/06/2010	0.113
		29/03/2010	1.283	29/05/2010	0.141	29/06/2010	0.111
		30/03/2010	2.024	30/05/2010	0.139	30/06/2010	0.109
		31/03/2010	1.335	31/05/2010	0.137		

Table Daily flow rate Glazert Water SEAPA

Station name: Milton of Campsie, Station number: 133114, External number: 84020
River: Glazert Water, Operator: SEPA, Easting: 265646, Northing: 676198

01/06/09	0.286	01/07/09	0.164	01/08/09	2.845	01/09/09	5.313	01/11/09	14.28
02/06/09	0.261	02/07/09	0.17	02/08/09	1.563	02/09/09	5.576	02/11/09	4.348
03/06/09	0.246	03/07/09	1.996	03/08/09	0.825	03/09/09	6.268	03/11/09	7.523
04/06/09	0.242	04/07/09	0.568	04/08/09	1.075	04/09/09	3.166	04/11/09	5.579
05/06/09	0.254	05/07/09	0.32	05/08/09	0.608	05/09/09	3.759	05/11/09	2.777
06/06/09	0.244	06/07/09	0.41	06/08/09	0.42	06/09/09	7.989	06/11/09	3.947
07/06/09	0.231	07/07/09	0.346	07/08/09	0.345	07/09/09	7.83	07/11/09	2.213
08/06/09	0.218	08/07/09	0.244	08/08/09	0.319	08/09/09	14.93	08/11/09	1.476
09/06/09	0.209	09/07/09	0.214	09/08/09	0.538	09/09/09	2.823	09/11/09	1.34
10/06/09	0.196	10/07/09	0.181	10/08/09	1.549	10/09/09	1.71	10/11/09	2.398
11/06/09	0.193	11/07/09	0.323	11/08/09	0.56	11/09/09	1.228	11/11/09	1.332
12/06/09	0.189	12/07/09	0.922	12/08/09	0.52	12/09/09	0.896	12/11/09	1.67
13/06/09	0.188	13/07/09	2.175	13/08/09	0.404	13/09/09	0.742	13/11/09	3.084
14/06/09	0.263	14/07/09	1.326	14/08/09	14.26	14/09/09	0.664	14/11/09	4.424
15/06/09	0.296	15/07/09	0.636	15/08/09	6.793	15/09/09	0.589	15/11/09	1.8
16/06/09	0.256	16/07/09	0.516	16/08/09	2.44	16/09/09	0.537	16/11/09	4.322
17/06/09	2.628	17/07/09	0.462	17/08/09	2.62	17/09/09	0.489	17/11/09	6.421
18/06/09	0.964	18/07/09	0.358	18/08/09	4.365	18/09/09	0.456	18/11/09	9.891
19/06/09	0.834	19/07/09	0.304	19/08/09	10.04	19/09/09	0.426	19/11/09	29.79
20/06/09	0.479	20/07/09	0.335	20/08/09	8.674	20/09/09	0.399	20/11/09	7.91
21/06/09	0.34	21/07/09	0.971	21/08/09	3.679	21/09/09	2.048	21/11/09	5.32
22/06/09	0.29	22/07/09	1.802	22/08/09	3.792	22/09/09	1.113	22/11/09	5.599
23/06/09	0.246	23/07/09	1.331	23/08/09	7.821	23/09/09	0.666	23/11/09	3.795
24/06/09	0.22	24/07/09	0.628	24/08/09	2.332	24/09/09	0.534	24/11/09	11.47
25/06/09	0.199	25/07/09	0.382	25/08/09	1.349	25/09/09	0.495	25/11/09	10.41
26/06/09	0.19	26/07/09	2.565	26/08/09	5.815	26/09/09	0.45	26/11/09	9.045
27/06/09	0.191	27/07/09	0.886	27/08/09	3.437	27/09/09	0.461	27/11/09	4.624
28/06/09	0.189	28/07/09	4.169	28/08/09	2.078	28/09/09	0.755	28/11/09	2.693
29/06/09	0.177	29/07/09	1.595	29/08/09	1.462	29/09/09	0.98	29/11/09	2.211
30/06/09	0.17	30/07/09	0.659	30/08/09	5.274	30/09/09	1.009	30/11/09	1.493
		31/07/09	1.822	31/08/09	11.84				

Daily flow rate Glazert water (SEAPA)

01/02/2010	0.568	01/03/2010	0.814	01/05/2010	0.383	01/06/2010	0.255
02/02/2010	0.758	02/03/2010	0.702	02/05/2010	0.351	02/06/2010	0.186
03/02/2010	0.593	03/03/2010	0.626	03/05/2010	0.319	03/06/2010	0.175
04/02/2010	1.046	04/03/2010	0.577	04/05/2010	0.295	04/06/2010	0.153
05/02/2010	2.609	05/03/2010	0.614	05/05/2010	0.29	05/06/2010	0.145
06/02/2010	2.6	06/03/2010	0.666	06/05/2010	0.282	06/06/2010	0.148
07/02/2010	1.38	07/03/2010	0.77	07/05/2010	0.262	07/06/2010	0.164
08/02/2010	0.864	08/03/2010	0.732	08/05/2010	0.244	08/06/2010	0.274
09/02/2010	0.645	09/03/2010	0.64	09/05/2010	0.24	09/06/2010	0.395
10/02/2010	0.562	10/03/2010	0.634	10/05/2010	0.23	10/06/2010	0.229
11/02/2010	0.498	11/03/2010	1.064	11/05/2010	0.225	11/06/2010	0.181
12/02/2010	0.465	12/03/2010	1.66	12/05/2010	0.225	12/06/2010	0.16
13/02/2010	0.435	13/03/2010	2.543	13/05/2010	0.279	13/06/2010	0.367
14/02/2010	0.452	14/03/2010	3.709	14/05/2010	0.266	14/06/2010	0.229
15/02/2010	0.886	15/03/2010	4.477	15/05/2010	0.229	15/06/2010	0.178
16/02/2010	0.585	16/03/2010	2.302	16/05/2010	0.225	16/06/2010	0.157
17/02/2010	0.481	17/03/2010	4.457	17/05/2010	0.21	17/06/2010	0.148
18/02/2010	0.404	18/03/2010	3.814	18/05/2010	0.229	18/06/2010	0.137
19/02/2010	0.368	19/03/2010	1.857	19/05/2010	0.232	19/06/2010	0.129
20/02/2010	0.344	20/03/2010	0.783	20/05/2010	0.224	20/06/2010	0.126
21/02/2010	0.313	21/03/2010	0.641	21/05/2010	0.21	21/06/2010	0.129
22/02/2010	0.286	22/03/2010	2.838	22/05/2010	0.194	22/06/2010	0.127
23/02/2010	0.316	23/03/2010	1.112	23/05/2010	0.185	23/06/2010	0.127
24/02/2010	1.42	24/03/2010	2.232	24/05/2010	0.176	24/06/2010	0.13
25/02/2010	5.188	25/03/2010	1.909	25/05/2010	0.186	25/06/2010	0.127
26/02/2010	3.946	26/03/2010	5.722	26/05/2010	0.168	26/06/2010	0.123
27/02/2010	1.967	27/03/2010	1.923	27/05/2010	0.166	27/06/2010	0.138
28/02/2010	1.187	28/03/2010	1.435	28/05/2010	0.168	28/06/2010	0.149
		29/03/2010	3.264	29/05/2010	0.177	29/06/2010	0.137
		30/03/2010	6.059	30/05/2010	0.168	30/06/2010	0.13
		31/03/2010	2.505	31/05/2010	0.164		

Table Daily flow rate Bothlin Burn SEAPA

Station name: Auchengeich, Station number: 133061,External number: 84023
River: Bothlin Burn, Operator: SEPA, Easting: 267977, Northing: 671609

01/06/09	0.138	01/07/09	0.073	01/08/09	0.349	01/09/09	1.122	01/11/09	3.722
02/06/09	0.128	02/07/09	0.092	02/08/09	0.266	02/09/09	1.315	02/11/09	1.994
03/06/09	0.123	03/07/09	0.244	03/08/09	0.232	03/09/09	2.837	03/11/09	2.112
04/06/09	0.12	04/07/09	0.11	04/08/09	0.196	04/09/09	1.631	04/11/09	1.721
05/06/09	0.117	05/07/09	0.089	05/08/09	0.152	05/09/09	1.328	05/11/09	1.332
06/06/09	0.111	06/07/09	0.164	06/08/09	0.12	06/09/09	1.179	06/11/09	1.254
07/06/09	0.101	07/07/09	0.11	07/08/09	0.111	07/09/09	1.139	07/11/09	1.135
08/06/09	0.092	08/07/09	0.09	08/08/09	0.109	08/09/09	2.38	08/11/09	0.874
09/06/09	0.089	09/07/09	0.078	09/08/09	0.399	09/09/09	1.285	09/11/09	0.802
10/06/09	0.088	10/07/09	0.071	10/08/09	0.648	10/09/09	0.92	10/11/09	0.987
11/06/09	0.085	11/07/09	0.202	11/08/09	0.443	11/09/09	0.691	11/11/09	0.801
12/06/09	0.081	12/07/09	0.169	12/08/09	0.457	12/09/09	0.558	12/11/09	0.703
13/06/09	0.081	13/07/09	0.35	13/08/09	0.34	13/09/09	0.475	13/11/09	0.963
14/06/09	0.088	14/07/09	0.325	14/08/09	2.644	14/09/09	0.428	14/11/09	1.362
15/06/09	0.148	15/07/09	0.278	15/08/09	2.674	15/09/09	0.375	15/11/09	0.93
16/06/09	0.098	16/07/09	0.598	16/08/09	1.195	16/09/09	0.335	16/11/09	1.155
17/06/09	0.214	17/07/09	0.311	17/08/09	0.996	17/09/09	0.306	17/11/09	1.592
18/06/09	0.2	18/07/09	0.247	18/08/09	0.795	18/09/09	0.276	18/11/09	2.104
19/06/09	0.116	19/07/09	0.212	19/08/09	1.119	19/09/09	0.255	19/11/09	4.935
20/06/09	0.093	20/07/09	0.179	20/08/09	1.83	20/09/09	0.233	20/11/09	3.794
21/06/09	0.083	21/07/09	0.274	21/08/09	1.226	21/09/09	0.264	21/11/09	2.69
22/06/09	0.08	22/07/09	0.252	22/08/09	0.944	22/09/09	0.226	22/11/09	2.823
23/06/09	0.074	23/07/09	0.208	23/08/09	1.313	23/09/09	0.207	23/11/09	2.49
24/06/09	0.071	24/07/09	0.197	24/08/09	0.939	24/09/09	0.194	24/11/09	2.957
25/06/09	0.068	25/07/09	0.145	25/08/09	0.705	25/09/09	0.174	25/11/09	3.77
26/06/09	0.072	26/07/09	0.276	26/08/09	0.874	26/09/09	0.161	26/11/09	2.717
27/06/09	0.069	27/07/09	0.188	27/08/09	0.746	27/09/09	0.158	27/11/09	2.189
28/06/09	0.07	28/07/09	0.499	28/08/09	0.674	28/09/09	0.155	28/11/09	1.724
29/06/09	0.075	29/07/09	0.391	29/08/09	0.576	29/09/09	0.174	29/11/09	1.479
30/06/09	0.07	30/07/09	0.243	30/08/09	0.61	30/09/09	0.171	30/11/09	1.187
		31/07/09	0.248	31/08/09	1.632				

Table Daily flow rate Bothlin Burn SEAPA

01/02/2010	0.348	01/03/2010	1.203	01/05/2010	0.277	01/06/2010	0.206
02/02/2010	0.446	02/03/2010	0.87	02/05/2010	0.267	02/06/2010	0.146
03/02/2010	0.369	03/03/2010	0.68	03/05/2010	0.241	03/06/2010	0.124
04/02/2010	0.437	04/03/2010	0.586	04/05/2010	0.229	04/06/2010	0.117
05/02/2010	0.687	05/03/2010	0.521	05/05/2010	0.234	05/06/2010	0.111
06/02/2010	0.81	06/03/2010	0.471	06/05/2010	0.225	06/06/2010	0.106
07/02/2010	0.611	07/03/2010	0.409	07/05/2010	0.208	07/06/2010	0.156
08/02/2010	0.534	08/03/2010	0.397	08/05/2010	0.197	08/06/2010	0.273
09/02/2010	0.489	09/03/2010	0.353	09/05/2010	0.193	09/06/2010	0.185
10/02/2010	0.393	10/03/2010	0.307	10/05/2010	0.186	10/06/2010	0.127
11/02/2010	0.337	11/03/2010	0.306	11/05/2010	0.183	11/06/2010	0.11
12/02/2010	0.314	12/03/2010	0.274	12/05/2010	0.18	12/06/2010	0.097
13/02/2010	0.306	13/03/2010	0.251	13/05/2010	0.22	13/06/2010	0.109
14/02/2010	0.322	14/03/2010	0.243	14/05/2010	0.214	14/06/2010	0.097
15/02/2010	0.467	15/03/2010	0.233	15/05/2010	0.204	15/06/2010	0.086
16/02/2010	0.396	16/03/2010	0.249	16/05/2010	0.201	16/06/2010	0.083
17/02/2010	0.346	17/03/2010	0.263	17/05/2010	0.19	17/06/2010	0.079
18/02/2010	0.309	18/03/2010	0.233	18/05/2010	0.181	18/06/2010	0.076
19/02/2010	0.272	19/03/2010	0.227	19/05/2010	0.208	19/06/2010	0.069
20/02/2010	0.243	20/03/2010	0.203	20/05/2010	0.213	20/06/2010	0.066
21/02/2010	0.227	21/03/2010	0.201	21/05/2010	0.204	21/06/2010	0.068
22/02/2010	0.199	22/03/2010	0.273	22/05/2010	0.176	22/06/2010	0.065
23/02/2010	0.203	23/03/2010	0.227	23/05/2010	0.151	23/06/2010	0.064
24/02/2010	0.726	24/03/2010	0.229	24/05/2010	0.145	24/06/2010	0.066
25/02/2010	3.134	25/03/2010	0.303	25/05/2010	0.146	25/06/2010	0.062
26/02/2010	3.069	26/03/2010	0.794	26/05/2010	0.142	26/06/2010	0.062
27/02/2010	2.293	27/03/2010	0.527	27/05/2010	0.165	27/06/2010	0.071
28/02/2010	1.631	28/03/2010	0.523	28/05/2010	0.147	28/06/2010	0.099
		29/03/2010	1.495	29/05/2010	0.144	29/06/2010	0.086
		30/03/2010	4.564	30/05/2010	0.139	30/06/2010	0.077
		31/03/2010	2.354	31/05/2010	0.143		

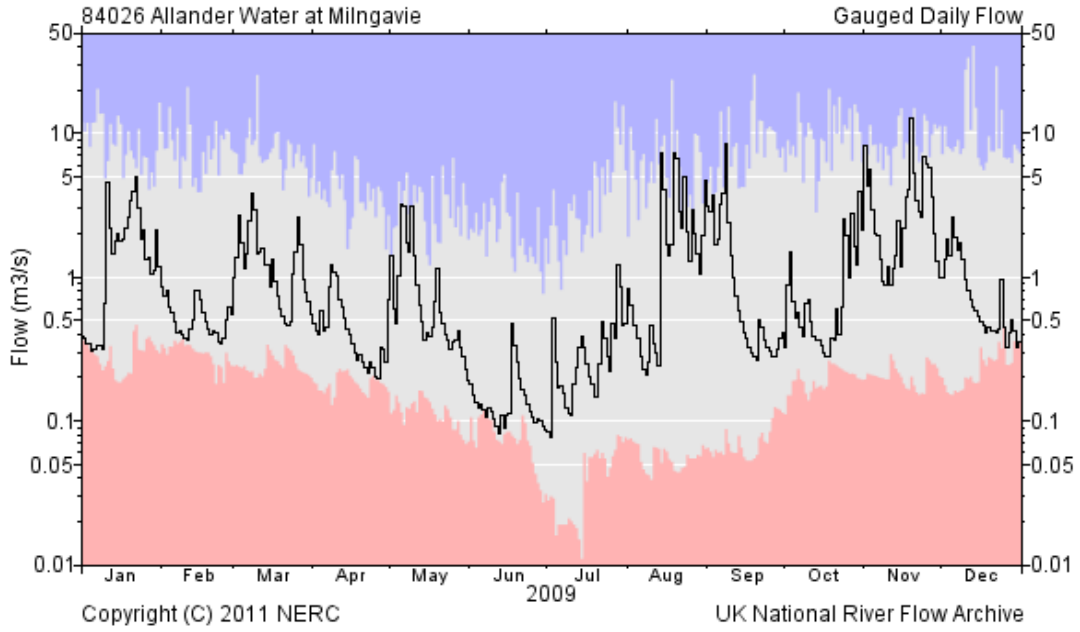
Table Daily flow rate Luggie Burn SEAPA

Station name: Condorrat, Station number: 133072, External number: 84016, River: Luggie Water, Operator: SEPA, Easting: 273915, Northing: 672560

01/06/09	0.181	01/07/09	0.131	01/08/09	0.654	01/09/09	1.464	01/11/09	7.544
02/06/09	0.173	02/07/09	0.132	02/08/09	0.463	02/09/09	2.095	02/11/09	2.345
03/06/09	0.171	03/07/09	0.162	03/08/09	0.308	03/09/09	5.248	03/11/09	2.598
04/06/09	0.176	04/07/09	0.127	04/08/09	0.26	04/09/09	1.853	04/11/09	1.76
05/06/09	0.183	05/07/09	0.141	05/08/09	0.203	05/09/09	1.586	05/11/09	1.205
06/06/09	0.195	06/07/09	0.54	06/08/09	0.18	06/09/09	1.387	06/11/09	1.22
07/06/09	0.162	07/07/09	0.212	07/08/09	0.237	07/09/09	1.388	07/11/09	1.07
08/06/09	0.155	08/07/09	0.177	08/08/09	0.384	08/09/09	3.582	08/11/09	0.78
09/06/09	0.152	09/07/09	0.161	09/08/09	2.284	09/09/09	1.452	09/11/09	0.74
10/06/09	0.15	10/07/09	0.125	10/08/09	1.636	10/09/09	0.965	10/11/09	1.06
11/06/09	0.148	11/07/09	0.252	11/08/09	0.777	11/09/09	0.735	11/11/09	0.77
12/06/09	0.145	12/07/09	0.212	12/08/09	0.798	12/09/09	0.597	12/11/09	0.70
13/06/09	0.146	13/07/09	0.648	13/08/09	0.524	13/09/09	0.508	13/11/09	1.18
14/06/09	0.238	14/07/09	0.322	14/08/09	4.565	14/09/09	0.44	14/11/09	2.12
15/06/09	0.307	15/07/09	0.307	15/08/09	3.867	15/09/09	0.385	15/11/09	1.09
16/06/09	0.166	16/07/09	0.852	16/08/09	1.257	16/09/09	0.337	16/11/09	1.68
17/06/09	0.429	17/07/09	0.506	17/08/09	1.052	17/09/09	0.319	17/11/09	2.31
18/06/09	0.353	18/07/09	0.302	18/08/09	0.809	18/09/09	0.307	18/11/09	3.34
19/06/09	0.192	19/07/09	0.229	19/08/09	1.476	19/09/09	0.287	19/11/09	8.57
20/06/09	0.162	20/07/09	0.188	20/08/09	2.559	20/09/09	0.274	20/11/09	4.24
21/06/09	0.152	21/07/09	0.279	21/08/09	1.471	21/09/09	0.311	21/11/09	2.93
22/06/09	0.148	22/07/09	0.233	22/08/09	1.212	22/09/09	0.276	22/11/09	3.37
23/06/09	0.14	23/07/09	0.218	23/08/09	2.411	23/09/09	0.259	23/11/09	2.47
24/06/09	0.137	24/07/09	0.247	24/08/09	1.261	24/09/09	0.25	24/11/09	3.31
25/06/09	0.134	25/07/09	0.232	25/08/09	0.774	25/09/09	0.25	25/11/09	4.91
26/06/09	0.134	26/07/09	0.479	26/08/09	1.272	26/09/09	0.234	26/11/09	2.49
27/06/09	0.133	27/07/09	0.237	27/08/09	1.226	27/09/09	0.23	27/11/09	1.76
28/06/09	0.134	28/07/09	0.855	28/08/09	0.945	28/09/09	0.237	28/11/09	1.26
29/06/09	0.129	29/07/09	0.562	29/08/09	0.679	29/09/09	0.292	29/11/09	1.13
30/06/09	0.126	30/07/09	0.283	30/08/09	0.841	30/09/09	0.26	30/11/09	0.88
		31/07/09	0.444	31/08/09	2.963				

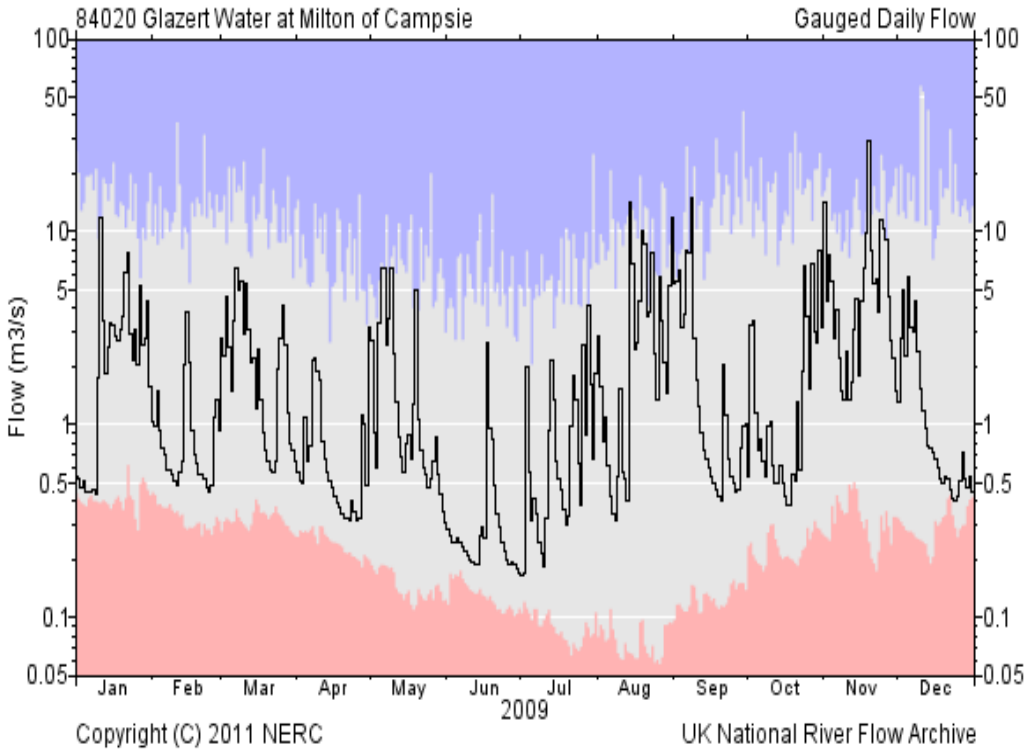
Table Daily flow rate Luggie Burn SEAPA

01/02/2010	0.428	01/03/2010	1.117	01/05/2010	0.29	01/06/2010	0.204
02/02/2010	0.572	02/03/2010	0.841	02/05/2010	0.271	02/06/2010	0.155
03/02/2010	0.428	03/03/2010	0.713	03/05/2010	0.243	03/06/2010	0.151
04/02/2010	0.655	04/03/2010	0.63	04/05/2010	0.233	04/06/2010	0.147
05/02/2010	1.184	05/03/2010	0.885	05/05/2010	0.238	05/06/2010	0.146
06/02/2010	1.407	06/03/2010	1.199	06/05/2010	0.23	06/06/2010	0.148
07/02/2010	0.906	07/03/2010	1.345	07/05/2010	0.214	07/06/2010	0.159
08/02/2010	0.759	08/03/2010	0.91	08/05/2010	0.204	08/06/2010	0.333
09/02/2010	0.598	09/03/2010	0.797	09/05/2010	0.201	09/06/2010	0.226
10/02/2010	0.469	10/03/2010	0.656	10/05/2010	0.197	10/06/2010	0.17
11/02/2010	0.394	11/03/2010	0.646	11/05/2010	0.191	11/06/2010	0.162
12/02/2010	0.376	12/03/2010	0.572	12/05/2010	0.189	12/06/2010	0.155
13/02/2010	0.364	13/03/2010	0.501	13/05/2010	0.271	13/06/2010	0.165
14/02/2010	0.382	14/03/2010	0.46	14/05/2010	0.217	14/06/2010	0.144
15/02/2010	0.614	15/03/2010	0.416	15/05/2010	0.203	15/06/2010	0.142
16/02/2010	0.479	16/03/2010	0.385	16/05/2010	0.197	16/06/2010	0.142
17/02/2010	0.397	17/03/2010	0.381	17/05/2010	0.182	17/06/2010	0.138
18/02/2010	0.361	18/03/2010	0.341	18/05/2010	0.18	18/06/2010	0.132
19/02/2010	0.324	19/03/2010	0.319	19/05/2010	0.194	19/06/2010	0.127
20/02/2010	0.301	20/03/2010	0.303	20/05/2010	0.184	20/06/2010	0.126
21/02/2010	0.285	21/03/2010	0.306	21/05/2010	0.175	21/06/2010	0.127
22/02/2010	0.257	22/03/2010	0.425	22/05/2010	0.168	22/06/2010	0.125
23/02/2010	0.268	23/03/2010	0.32	23/05/2010	0.167	23/06/2010	0.13
24/02/2010	0.879	24/03/2010	0.35	24/05/2010	0.163	24/06/2010	0.128
25/02/2010	4.14	25/03/2010	0.512	25/05/2010	0.158	25/06/2010	0.125
26/02/2010	5.841	26/03/2010	1.48	26/05/2010	0.16	26/06/2010	0.125
27/02/2010	2.569	27/03/2010	0.807	27/05/2010	0.168	27/06/2010	0.144
28/02/2010	1.617	28/03/2010	0.811	28/05/2010	0.164	28/06/2010	0.19
		29/03/2010	3.286	29/05/2010	0.177	29/06/2010	0.133
		30/03/2010	6.962	30/05/2010	0.158	30/06/2010	0.133
		31/03/2010	2.479	31/05/2010	0.17		



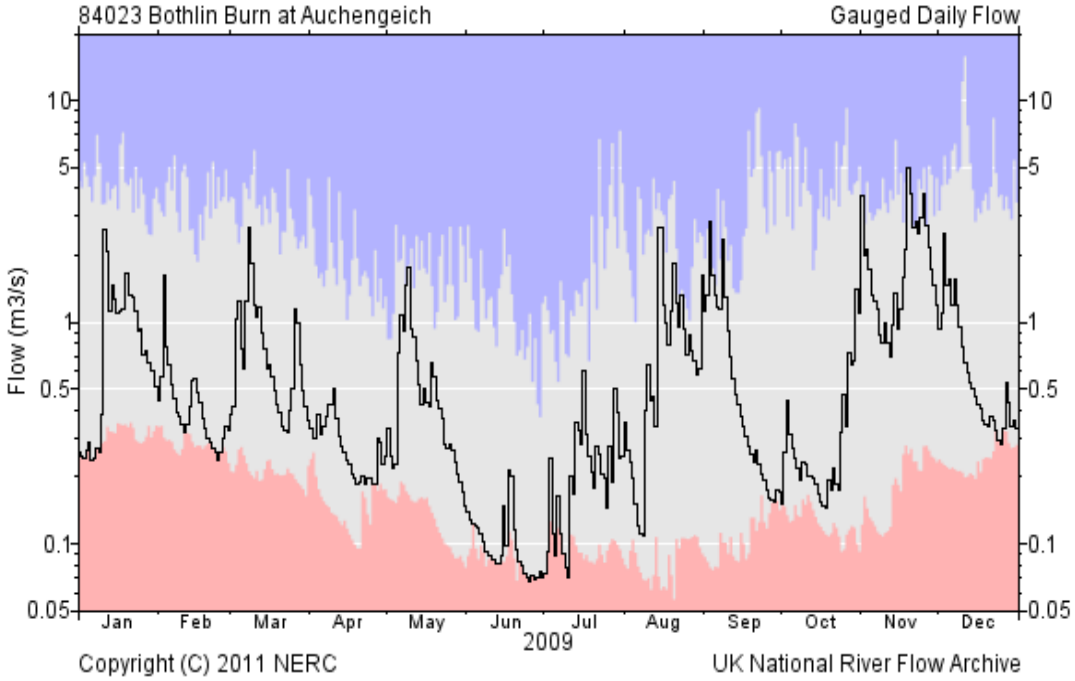
Allander

Period of Record:	1974 - 2009
Percent Complete:	99 %
Base Flow Index:	0.35
Mean Flow:	1.317 m^3/s
95% Exceedance (Q95):	0.129 m^3/s
70% Exceedance (Q70):	0.375 m^3/s
50% Exceedance (Q50):	0.681 m^3/s
10% Exceedance (Q10):	3.151 m^3/s



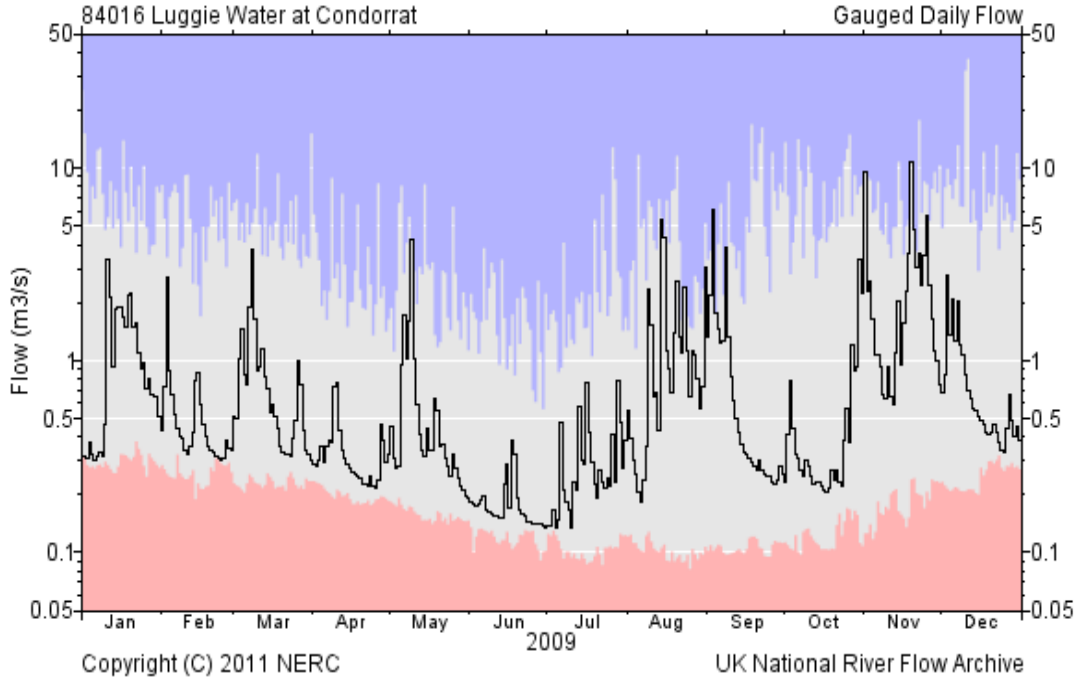
Glazert

Period of Record:	1968 - 2009
Percent Complete:	98 %
Base Flow Index:	0.3
Mean Flow:	2.081 m^3/s
95% Exceedance (Q95):	0.185 m^3/s
70% Exceedance (Q70):	0.513 m^3/s
50% Exceedance (Q50):	1.031 m^3/s
10% Exceedance (Q10):	5.137 m^3/s



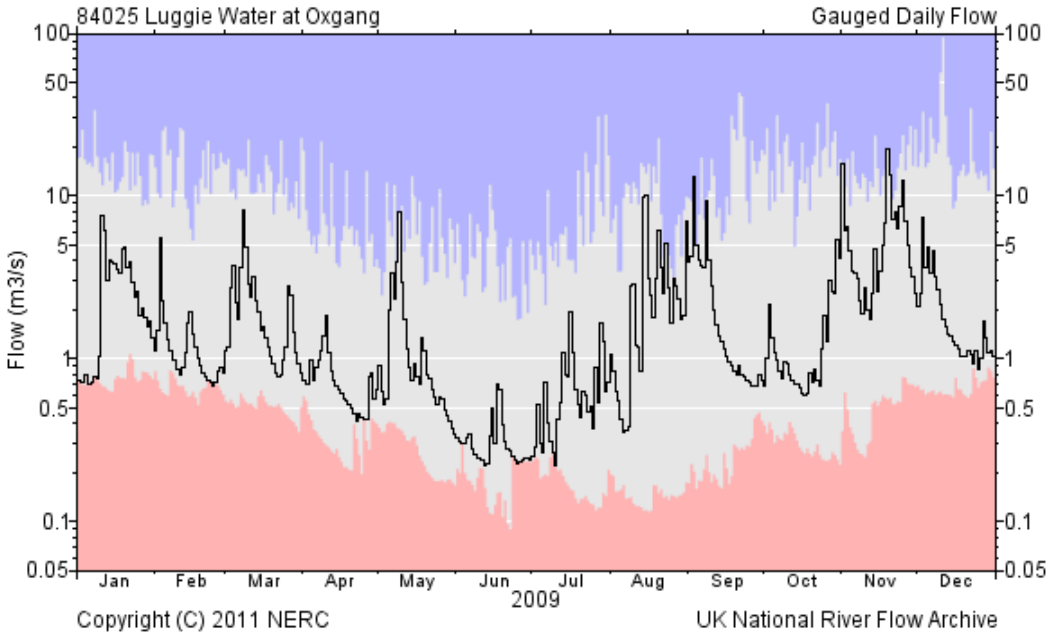
Bothlin

Period of Record:	1973 - 2009
Percent Complete:	95 %
Base Flow Index:	0.5
Mean Flow:	0.773 m^3/s
95% Exceedance (Q95):	0.143 m^3/s
70% Exceedance (Q70):	0.299 m^3/s
50% Exceedance (Q50):	0.465 m^3/s
10% Exceedance (Q10):	1.771 m^3/s



Luggie at Condorrat

Period of Record:	1966 - 2009
Percent Complete:	95 %
Base Flow Index:	0.4
Mean Flow:	0.872 m^3/s
95% Exceedance (Q95):	0.145 m^3/s
70% Exceedance (Q70):	0.283 m^3/s
50% Exceedance (Q50):	0.471 m^3/s
10% Exceedance (Q10):	1.957 m^3/s



Period of Record:	1975 - 2009
Percent Complete:	>99 %
Base Flow Index:	0.41
Mean Flow:	2.391 m^3/s
95% Exceedance (Q95):	0.306 m^3/s
70% Exceedance (Q70):	0.766 m^3/s
50% Exceedance (Q50):	1.26 m^3/s
10% Exceedance (Q10):	5.633 m^3/s

Luggie at Oxgang

http://www.ceh.ac.uk/data/nrfa/data/search.html